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A 3-year research project was initiated to develop a portable, miniature, sorbent-type collection system for sampling and preconcentrating organics in general, and carcinogens and associated compounds (e.g., mutagens, precarcinogens, and cofactors) in particular, from ambient air. The purpose of such a system is to assess the exposure of individuals and/or small groups of individuals to these types of compounds in various environments. Inherent in the ability to assess exposures is not only the sampling capability but also analytical confirmation. The determinative step in this project will be capillary gas chromatography/mass spectroscopy.

Progress during the first year was discussed and concerned the selection of candidate sorbent materials; the selection of test compounds for sorbent evaluation; the evaluation of the sorbent materials in terms of capacity, desorption properties, and physical properties that relate to pressure drops and ultimate system design, and the selection of a three-sorbent system based on Tenax-GC, Porapak R, and Ambersorb.

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Portable Miniature Sampler for Potential Airborne Carcinogens in Microenvironments

Phase 1 Development

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PORTABLE MINIATURE SAMPLER FOR POTENTIAL AIRBORNE CARCINOGENS IN MICROENVIRONMENTS

Phase 1. Development

by

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ABSTRACT

A 3-year research program was initiated for the purpose of developing a portable, miniature, sorbent-type collection system for sampling and preconcentrating organics in general, and carcinogens and associated compounds (e.g., mutagens, precarcinogens, and cofactors) in particular, from ambient air. The purpose of such a system is to assess the exposure of individuals and/or small groups of individuals to these types of compounds in various environments. Inherent in the ability to assess exposures is not only the sampling capability but also analytical confirmation. The determinative step in this program will be capillary gas chromatography/mass spectroscopy.

Progress during the first year is discussed and deals with the selection of candidate sorbent materials; the selection of test compounds for sorbent evaluation; the evaluation of the sorbent materials in terms of capacity, desorption properties, and physical properties that relate to pressure drops and ultimate system design; the selection of a three-sorbent system based on Tenax-GC, Porapak R, and Ambersorb XE-340; and the consideration of various design parameters for the pump and system hardware.

The selection of Tenax-GC, Porapak R, and Ambersorb XE-340 was based on the need to have a system that would be capable of sampling a broad range of organic compounds in terms of volatility and polarity and still be amenable to recovery processes, particularly thermal desorption. Other sorbents evaluated during this process were Porapak N and SKC activated coconut charcoal. The

test compounds used to evaluate sorbent characteristics included n-butane, benzene, propylene oxide, benzyl chloride, acrylonitrile, phenol, iso-octane, naphthalene, bis(2-chloroethyl) ether, 1,2,4-trichlorobenzene, ethylene glycol, *m*-nitroanisole, n-hexadecane, phenanthrene, hexachloro-1,3-butadiene, 4-bromodiphenyl ether, succinotrile, and *o*-nitroaniline.

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SECTION 1

INTRODUCTION

A wide variety of gases, vapors and particulates of organic compounds, ranging from volatile hydrocarbons (e.g. methane) to high molecular weight phthalates (plasticizers), polychlorinated biphenyls (pesticides), and polynuclear aromatics, are present within the atmosphere. Some of these organic compounds have been shown or are suspected to be carcinogens, mutagens, cofactors, or precursors and therefore are of environmental and health concern. The objective of this three-year project is to develop a portable miniature collection system capable of concentrating a wide variety of organic compound vapors from ambient air. This system is then to be evaluated for assessing the exposure of an individual or small group of individuals to carcinogens, mutagens, cofactors, precursors, and the like.

The text of this report focuses on the work conducted during the first year of this project. This work included the survey, evaluation, and selection of adsorbent materials for use within the portable miniature collection system and the initial development of this collection system.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Five solid sorbent materials were selected from the variety of sorbent materials commercially available based upon information obtained through a literature survey. These sorbents were then evaluated with a matrix of eighteen test organic compounds selected to represent a wide range of volatilities, polarities, and functionalities. Based upon laboratory evaluations of the capacity, desorption efficiency, background, decomposition, and pressure drop properties of these five sorbents, a combination of three was selected for use within a portable miniature air collection system. The three sorbents selected were Tenax-GC, Porapak R, and Ambersorb XE-340 which should be useful for the collection/analysis of low volatility, intermediate volatility, and high volatility compounds, respectively.

Tapered glass tubes of specific dimensions were determined to be the best means of containing the sorbents and a basic sampling system was designed, which consisted of three sorbent-filled glass tubes in a series or parallel arrangement, followed by optional flow control/measurement equipment (needle valves and rotameters), and ending with a portable, battery-operated pump.

Future research will include an evaluation of the design options of this basic sampling system and validation of its use in assessing the exposure of an individual or small group of individuals to carcinogens and related compounds through laborabory and field testing.

SECTION 3

TECHNICAL PROGRESS - PHASE I

TASK 1 - INITIAL RESEARCH

Literature Survey

Before initiating studies to evaluate and select sorbent materials, a comprehensive review of available literature on the use of solid sorbent materials for sampling organic vapors was conducted. Information was collected on specific sampling applications for over 110 compounds using more than 30 different sorbent materials. The pertinent knowledge obtained from this review included:

- Capacity/efficiency information for various compounds on various sorbents.
- A variety of desorption techniques, thermal and solvent.
- General knowledge of sorbent properties, capabilities, and problems.
- Sorbent conditioning procedures.
- Possible experimental techniques for sorbent evaluation and sampling validation.

Selection of Candidate Sorbent Materials

At least three and not more than six commercially available sorbent materials were to be selected for further laboratory evaluation based on information obtained through the literature survey. This survey indicated three major classes of sorbent materials, which are listed below with representatives of each class.

(1) Porous polymers - Tenax-GC
Porapaks
Chromosorbs
XAD's

(2) Carbonaceous materials - Activated carbons and charcoals
Graphitized carbon black
Ambersorbs

(3) Others - Molecular sieves
Silica gel
Liquid coated solid supports

Generally, the porous polymers were found to have the most desirable properties for air sampling, including low background and low reactivity, as well as high capacities for many compounds. Unfortunately, the porous polymers were found to have little capacity for the more volatile compounds. On the other hand, the carbonaceous materials were noted to have much better capacities for volatile compounds, but are plagued with reactivity problems and problems associated with hydrophilicity. The other sorbent materials generally had intermediate capacities and various associated sampling problems, and they have not been widely utilized in air sampling applications. Specific sorbents were selected from these three groups of sorbent materials.

The goal of this selection was to choose a collection of commercially available materials that, when used in an appropriate combination, showed promise for quantitatively trapping compounds varying widely in volatilities and polarities. To do this it was necessary to compare the trapping capabilities (capacities) of a sorbent for various compounds with parameters that are indicative of volatility and polarity. Plots were made of several volatility versus polarity parameters for a collection of compounds. Sorbent capacities for specific compounds were then superimposed on these plots to determine whether or not there were consistent trends in the trapping abilities of a sorbent related to these compound parameters.

Consistent trends in sorbent capacities were seen when related to compound volatilities as indicated by either vapor pressure or boiling point, with boiling point being the more convenient parameter. Unfortunately, finding a single polarity parameter that resulted in consistent sorbent capacity trends was not as easy. For example, Figure 1 is a plot of boiling point versus dipole moment for the compounds listed in Table 1. When capacity data (numbers next to the circled points in Figure 1) were superimposed on this plot, there were discontinuities in the data so that no clear trend was evident for sorbent capacities. It was felt that the inconsistencies in relating capacities to compound parameters in this plot lay in an inadequate method of expressing polarity. Therefore, other parameters (solubility parameter, hydrogen-bonding index, and polarity index) that have been used as measures of polarity were evaluated. Plots similar to Figure 1 were made in an attempt to relate volatility and capacity data to each of these parameters, but no good correlation was found for any single parameter.

It was possible, however, to make a qualitative evaluation of the relative merit of each of these parameters for relating the

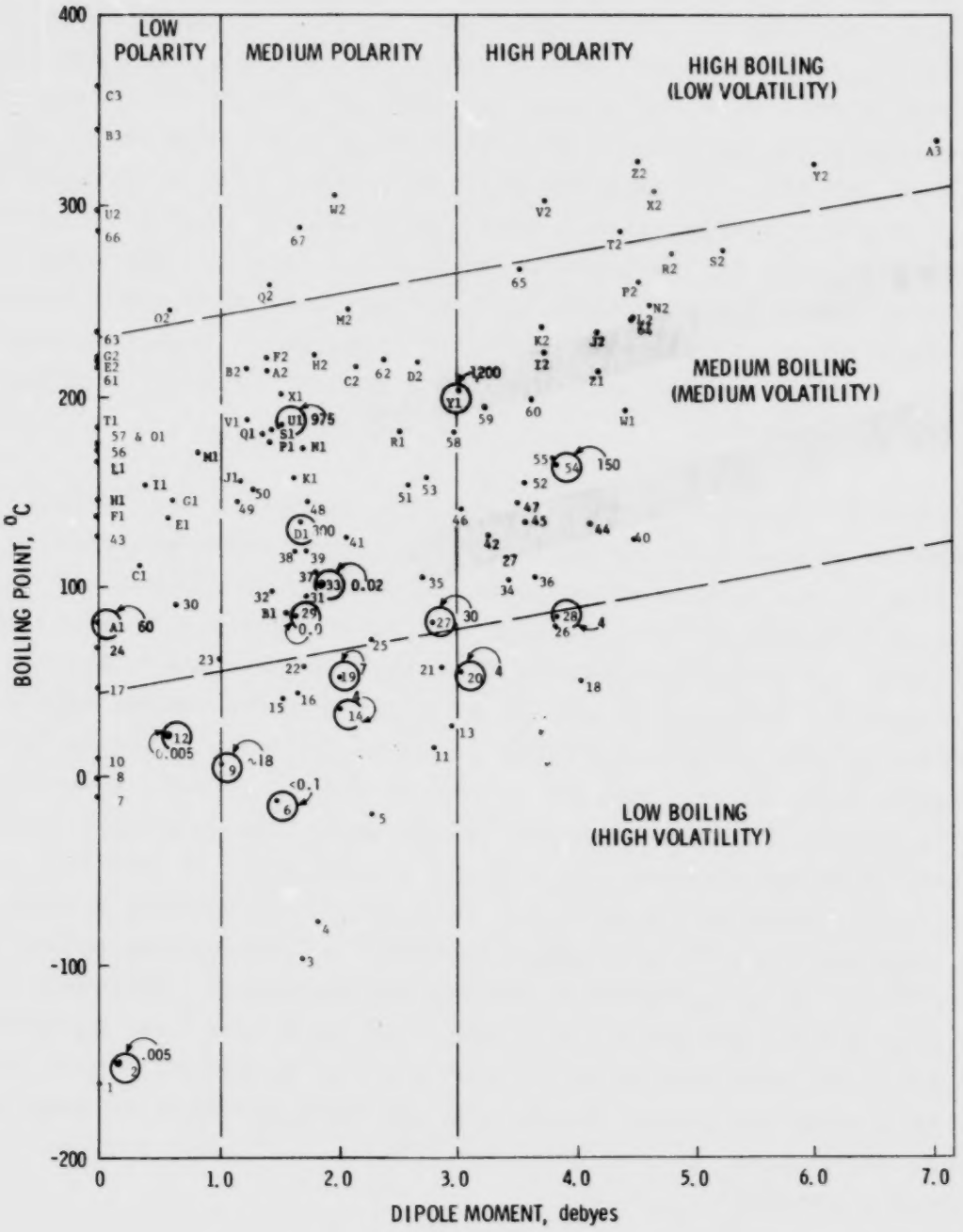

Figure 1. Capacity data for selected compounds on Tenax-GC superimposed on boiling point vs. dipole moment plot (entries correspond to compounds in Table 1).

TABLE 1. COMPOUNDS INCLUDED IN VOLATILITY POLARITY PLOTS (FIGURES 1, 2, AND 3)

Key[a]	Compound	Key[a]	Compound	Key[a]	Compound
Aliphatic (and inorganic):					
1	Methane	24	n-Hexane	47	1-Chloro-1-nitropropane
2	Nitrogen oxide	25	2,2-Dichloropropane	48	Isoamylacetate
3	Methanol	26	Acrylonitrile	49	n-Butyl ether
4	Fluoromethane	27	Methyl ethyl ketone	50	1,2,-Dibromo-2-methylpropane
5	Formaldehyde	28	Acetonitrile	51	2-Heptanone
6	Vinyl chloride	29	*t*-Butanol	52	1-Nitrobutane
7	Isobutane	30	Triethylamine	53	Cyclohexanone
8	n-Butane	31	2,3-Dichloropropene	54	β-Propiolactone
9	Dimethylamine	32	1,2-Dichloropropane	55	Dimethylacetamide
10	Neopentane	33	Water	56	*t*-Butylcyclohexane
11	Cyanogen chloride	34	Nitromethane	57	n-Decane
12	Nitrogen dioxide	35	3-Pentanone	58	Ethyl acetoacetate
13	Hydrogen cyanide	36	Crotonaldehyde	59	Formamide
14	1,2-Propylene oxide	37	1,3-Dichloropropene	60	Trimethylphosphate
15	Methylene chloride	38	n-Butanol	61	n-Dodecane
16	Methyl iodide	39	Acetic acid	62	Diethyl succinate
17	Carbon disulfide	40	Crotonitrile	63	n-Tridecane
18	Propionitrile	41	1,3-Dichloropropane	64	Dimethyl sulfone
19	1,3-Propylene oxide	42	1-Chloro-1-nitroethane	65	Succinonitrile
20	Acrolein	43	n-Octane	66	n-Hexadecane
21	Acetone	44	Valeronitrile	67	1,2,3,4,4,6-Hexachlorocyclohexane
22	Methyl acetate	45	Nitropropane		
23	Chloroform	46	Acetylacetone		
Aromatic:					
A1	Benzene	S1	Phenol	K2	*m*-Chloronitrobenzene
B1	Fluorobenzene	T1	*p*-Diethylbenzene	L2	*p*-Nitrotoluene
C1	Toluene	U1	Aniline	M2	Pyrocatechol
D1	Chlorobenzene	V1	Iodobenzene	N2	*o*-Chloronitrobenzene
E1	Ethylbenzene	W1	Benzonitrile	O2	1,2,3,5-Tetrachlorobenzene
F1	*p*-Xylene	X1	*p*-Cresol	P2	*m*-Nitroanisole
G1	*o*-Xylene	Y1	Acetophenone	Q2	Diphenyl ether
H1	Styrene	Z1	Nitrobenzene	R2	*o*-Nitroanisole
I1	Isopropylbenzene	A2	2,6-Dimethylphenol	S2	*p*-Nitroanisole
J1	Anisole	B2	1,2,4-Trichlorobenzene	T2	*o*-Nitroaniline
K1	Bromobenzene	C2	*m*-Chlorophenol	U2	*p*-Dinitrobenzene
L1	Mesitylene	D2	*p*-Chlorophenol	V2	*m*-Dinitrobenzene
M1	*t*-Butylbenzene	E2	Naphthalene	W2	4-Bromodiphenyl ether
N1	*m*-Dichlorobenzene	F2	*m*-Dibromobenzene	X2	*m*-Nitroaniline
O1	*p*-Dichlorobenzene	G2	*p*-Dibromobenzene	Y2	*o*-Dinitrobenzene
P1	*o*-Chlorophenol	H2	*o*-Dibromobenzene	Z2	4-Nitrodiphenyl ether
Q1	Benzyl chloride	I2	*o*-Nitrotoluene	A3	*p*-Nitroaniline
R1	*o*-Dichlorobenzene	J2	*m*-Nitrotoluene	B3	Phenanthrene
				C3	*m*-Diphenylbenzene

[a]The numbers in Figures 1, 2, and 3 correspond to these numbers. Compounds are listed in order of increasing boiling points.

capacity and volatility data to polarity. We judged the hydrogen-bonding index to be twice as good as the dipole moment and solubility parameters, while the polarity index was only about half as good. In addition, it was noted that compounds with similar functionalities generally had similar values for each of the measures of polarity examined.

These observations formed the basis for a rating scheme which gave a "composite" or relative polarity for the various functionalities. The rating was accomplished as follows. First the various functionalities were rated for each measure of polarity as having a high, moderately high, moderate, moderately low, or low value. This was done by determining the total range covered by each parameter and qualitatively assigning a relative value for a particular functionality depending upon where the values for compounds having that functionality fell within that range. Second, the measures of polarity were weighted according to how well they correlated with the capacity data. Table 2 contains the point value given for each combination in this weighting scheme. Third, the point values for all the polarity parameters were summed for each functionality to give a total "score." These scores formed the basis for placing the functionalities on the relative polarity scale that is used as the abcissa in Figures 2 and 3.

TABLE 2. "SCORING" SYSTEM FOR POLARITY EVALUATION

Value	Hydrogen bonding	Dipole moment	Solubility parameter	Polarity index
High	20	10	10	5
Moderately high	16	8	8	4
Moderate	12	6	6	3
Moderately low	8	4	4	2
Low	4	2	2	1

Figure 2 is a plot of boiling point versus functionality on the relative polarity scale described above for selected compounds. The capacities for certain of these compounds on Tenax were superimposed in bold numbers next to the corresponding points. Figure 3 is the same plot with capacities for certain compounds on Chromosorb 104 superimposed. The results showed that there is a good correlation between capacity data and a volatility/polarity plot of this nature. This was shown by consistent trends in the capacity data in moving vertically (i.e., from high to low volatility) or horizontally (i.e., from low to high polarity) on the plot.

It was possible to estimate lines of constant capacity. Two such estimates are represented by the shaded areas in Figures 2 and 3. The top shaded area in each plot represents the lower limit for the quantitative sampling of low levels (probably ppb or less) of compounds at a rate of 4 ℓ/min for 8 hours. This means that any compound falling in this shaded area or above would probably be quantitatively sampled under these conditions. The bottom shaded area represents the lower limit for quantitatively sampling low levels of compounds at a rate of 15 mℓ/min for 8 hours. This shows that a slower sampling rate results in the quantitative sampling of a broader range of compounds. It should be noted that these were only rough approximations based on limited data available in the literature.

Six sorbent materials were selected for further evaluation on the basis of these and similar plots and other considerations where there were insufficient data to construct a plot. These included Tenax-GC, Chromosorb 104, Porapak R, Porapak N, Ambersorb XE-340, and SKC coconut activated charcoal. Tenax-GC was selected for the collection of moderately high to high boiling compounds, since it has a high temperature limit. Tenax also has a slight preference for nonhydrogen bonding compounds. On the other hand, Chromosorb 104 was thought to prefer hydrogen-bonding compounds which are moderately high boiling. For moderately boiling

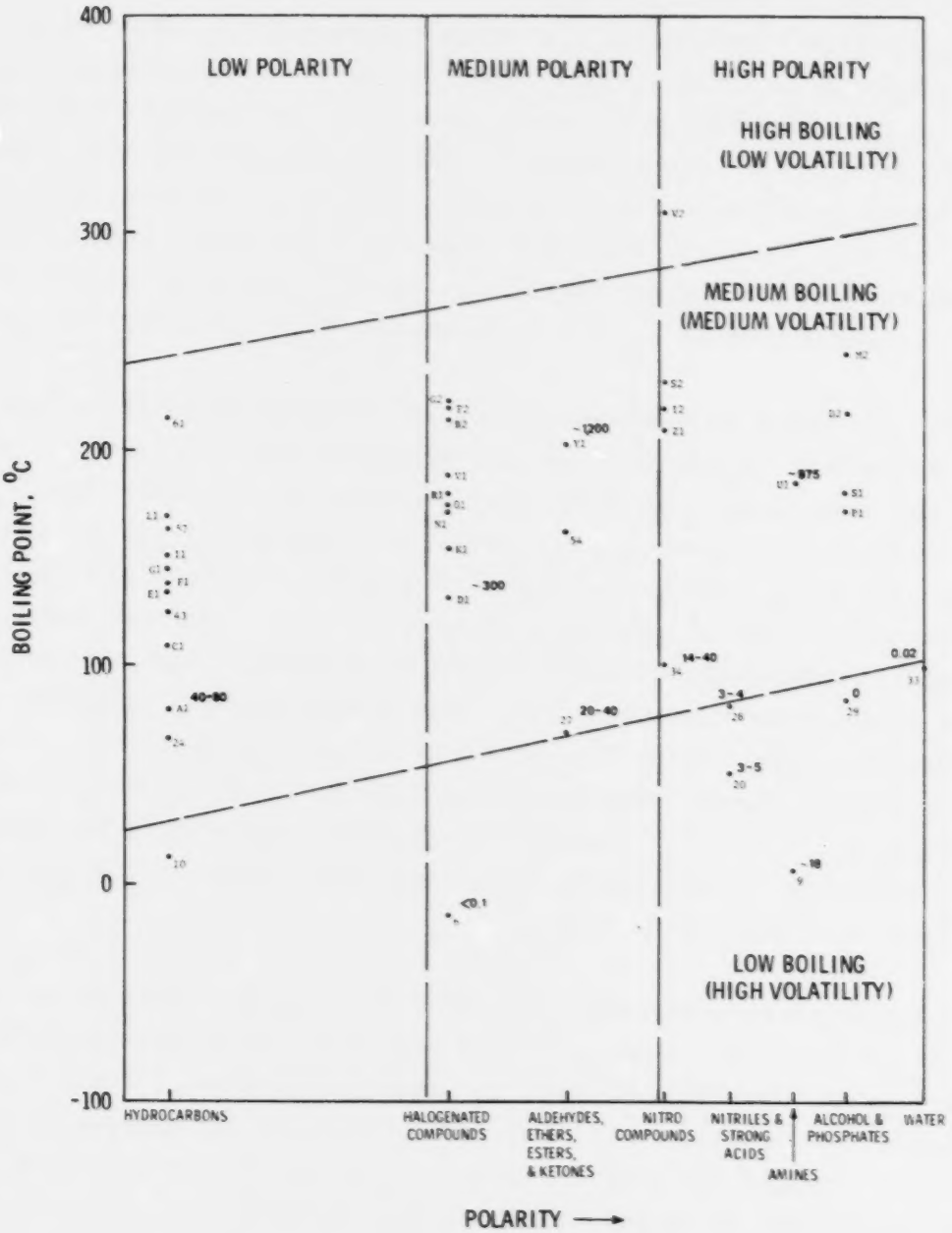

Figure 2. Capacity data for selected compounds on Tenax-GC superimposed on boiling point vs. relative polarity plot. (Entries correspond to compounds in Table 1.)

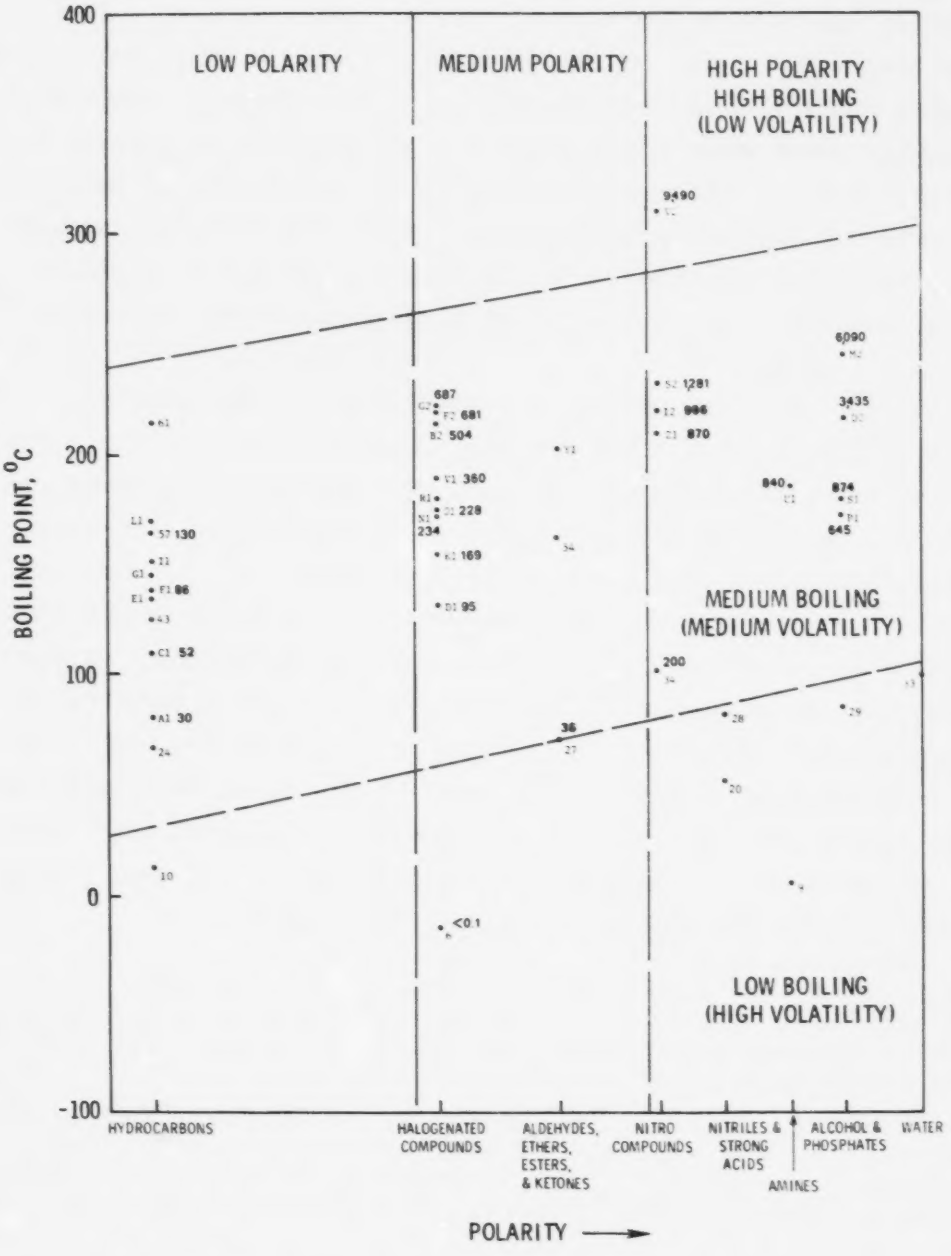

Figure 3. Capacity data for selected compounds on Chromosorb 104 superimposed on boiling point vs. relative polarity plot. (Entries correspond to compounds in Table 1.)

compounds, the literature showed Porapak R to have the greatest capacity, although retention time data indicated that Porapak N (for which there were no capacity data) might actually have greater capacity. For low boiling compounds, a wide variety of activated carbons had been used in the literature. However, the most common ones were those that had only moderate capacity. Moderate capacity charcoals seemed to be necessary in order to facilitate satisfactory desorption. Problems with activated carbons included difficulty of cleanup, significant humidity effects, and induced reactions of highly reactive compounds.

We decided to look at one activated charcoal, SKC coconut, and a new product line, the Rohm and Haas Ambersorb materials. The Ambersorbs are intermediate between the activated carbons and polymeric adsorbents and show promising capacities for highly volatile compounds (e.g., 81 ℓ/g for butane) [1]. These six sor- represent four porous polymers and two carbonaceous materials with a variety of individual properties and the potential, in some combination, to effectively sample compounds of a wide range of polarities and volatilities. Later, Chromosorb 104 was eliminated from consideration since it has been reported to have hydrophili- city problems [2], and higher background properties than Tenax-GC [3]. In addition, it would not be expected to add any capabilities to those offered by the Tenax and Porapak materials.

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[1] Holzer, G., H. Shanfield, A. Zlatkis, W. Bertsch, P. Juarez, H. Mayfield, and H. M. Lieblich. Collection and Analysis of Trace Organic Emissions from Natural Sources. Journal of Chromatography, 142:755-764, 1977.

[2] Pellizzari, E. D., J. E. Bunch, R. E. Berkley, and J. McRae. Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres. The Performance of a Tenax GC Cartridge Sampler for Hazardous Vapors. Analytical Letters, 9(1):45-63, 1976.

[3] Pellizzari, E. D., R. H. Carpenter, J. E. Bunch, and E. Sawicki. Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres. Thermal Desorption of Organic Vapors from Sorbent Media. Environmental Science & Technology, 9(6):556-560, 1975.

Selection of Test Compounds

To evaluate the selected sorbent materials for their sampling capabilities, it was necessary to establish a matrix of test compounds that sufficiently described the ranges of volatilities and polarities that were anticipated in this program. The matrix shown in Table 3 was established as a guide to the selection of appropriate test compounds.

TABLE 3. TEST COMPOUND MATRIX

	Low polarity	Medium polarity	High polarity
Aliphatic:			
Low volatility	x	x	x
Medium volatility	x	x	x
High volatility	x	x	x
Aromatic:			
Low volatility	x	x	x
Medium volatility	x	x	x
High volatility	x	x	x

The volatility/polarity plots of various compounds shown in Figures 2 and 3 were used to choose a number of tentative compounds for each of the matrix points. Factors used in the final selection were:

- The appearance of the compounds in the literature surveyed.
- The availability of the compounds.
- The variation of functionalities within the group selected.
- A suspected or known carcinogenicity of the compounds or similar compounds (but this was not a critical consideration).

The aliphatic and aromatic compounds that were finally chosen are given in Tables 4 and 5, respectively.

TASK 2 - SORBENT EVALUATION

Capacity Studies

The evaluation of the sorbent materials (Tenax-GC, Porapak R, Porapak N, Ambersorb XE-340, and SKC activated charcoal) began with studies of the abilities of these sorbents to quantitatively trap various organic compounds. Capacities were determined for as many of the 18 test matrix compounds as possible on each of the 5 sorbents. Additionally, some low molecular weight aliphatics (methane, ethane, propane, pentane, and hexane) were used to evaluate the carbonaceous sorbents, Ambersorb XE-340 and SKC activated charcoal, for their abilities to trap extremely volatile materials.

The experimental technique that was used to estimate sorbent capacities is a commonly cited, gas chromatographic technique involving the generation of Arrhenius plots. This technique involved packing chromatographic columns [0.9 m (3 ft) long, 0.6 cm (1/4 in.) O.D., 2 mm I.D.] with known weights of each of the five sorbent materials and conditioning these columns according to the specifications of the sorbent manufacturer. A column was then placed within a gas chromatograph and set at its highest allowable temperature under a flow of 30 mℓ/min of nitrogen. Samples of the test matrix and/or low molecular weight aliphatic compounds were then injected into the column and detected by a flame ionization detector (FID). Sample sizes were within the Henry's law region such that retention times were not affected by variations. The data obtained included the retention time (RT) which was considered to be the amount of time from injection to peak maximum and the first elution time (FET) which was the time from injection to peak initiation. These points are indicated in

TABLE 4. MATRIX OF ALIPHATIC TEST COMPOUNDS

Volatility	Polarity: Hydrocarbons (Low)	Halogenated compounds, aldehydes, ethers, ketones and esters (Medium)	Nitro compounds, nitriles, amines, and strong acids, alcohols and phosphates (High)
Low	n-Hexadecane (bp 205+°C)[a]	Hexachloro-1,3-butadiene (bp 215+°C)	Succinonitrile (bp 225+°C)
Medium	iso-Octane (bp 120-175°C)	Bis(2-chloroethyl) ether (bp 135-185°C)	Ethylene glycol (bp 150-200°C)
High	n-Butane (bp <50°C)	Propylene oxide (bp <65°C)	Acrylonitrile (bp <90°C)

[a]Temperatures in parentheses represent boiling point values used as criteria for inclusion in the various volatility classes (low, medium, high).

TABLE 5. MATRIX OF AROMATIC TEST COMPOUNDS

Volatility	Polarity: Hydrocarbons (Low)	Halogenated compounds, aldehydes, ethers, ketones and esters (Medium)	Nitro compounds, nitriles, amines, and strong acids, alcohols and phosphates (High)
Low	Phenanthrene (bp 250+°C)[a]	4-Bromodiphenyl ether (bp 255+°C)	Nitroaniline (bp 280+°C)
Medium	Naphthalene (bp 200-245°C)	1,2,4-Trichlorobenzene (bp 210-250°C)	Nitroanisole (bp 230-260°C)
High	Benzene (bp <165°C)	Benzyl chloride (bp <180°C)	Phenol (bp <210°C)

[a]Temperatures in parentheses represent boiling point values used as criteria for inclusion in the various volatility classes (low, medium, high).

Figure 4. By multiplying the retention times and first elution times by the flow rate and dividing by the amount of sorbent within the chromatographic column the 50% ($^{50\%}Vg$) and FET (^{FET}Vg) volumetric capacities, respectively, were obtained. Sample injections were then made at a variety of column temperatures to obtain similar data.

An example of the experimental information obtained with Porapak R is given in Table 6. These data were used to obtain an Arrhenius plot (log Vg vs. 1/T where T = absolute temperature). Figures 5 and 6 are examples of these plots for the $^{50\%}Vg$ and ^{FET}Vg values, respectively, for Porapak R. The ^{FET}Vg values were then extrapolated to 20°C to obtain the approximate ambient volumetric capacities ($^{FET}Vg_{20°C}$) of this sorbent for the test compounds. Table 7 gives this information for Porapak R.

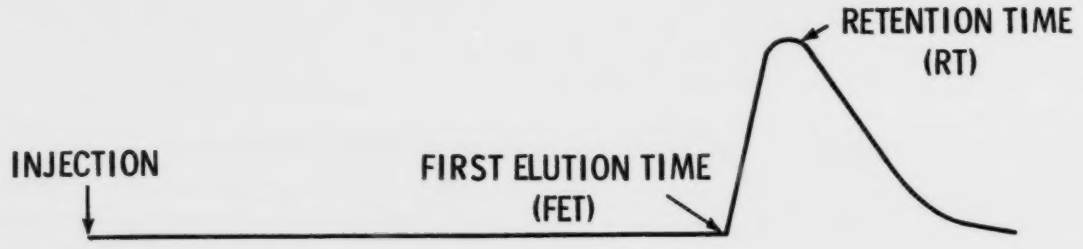

Figure 4. Elution analysis method for sorbent capacity determination.

TABLE 7. CAPACITIES FOR SELECTED TEST COMPOUNDS ON PORAPAK R

Compound name	^{FET}Vg, ℓ/g
n-Butane	4.93
Propylene oxide	12.4
Acrylonitrile	16.8
iso-Octane	3,550
Benzene	175

TABLE 6. RETENTION TIMES AND CAPACITIES FOR SELECTED TEST COMPOUNDS ON PORAPAK R

Temperature, °C	Compound				
	n-Butane	Propylene oxide	Acrylonitrile	iso-Octane	Benzene
222	RT = 0.17 min $^{50\%}V_g$ = 8.22 x 10^3 ℓ/g FET = 0.04 min FET_{Vg} = 1.94 x 10^3 ℓ/g	RT = 0.20 min $^{50\%}V_g$ = 9.68 x 10^3 ℓ/g FET = 0.05 min FET_{Vg} = 2.42 x 10^3 ℓ/g	RT = 0.24 min $^{50\%}V_g$ = 11.6 x 10^3 ℓ/g FET = 0.12 min FET_{Vg} = 5.81 x 10^3 ℓ/g	RT = 0.85 min $^{50\%}V_g$ = 41.1 x 10^3 ℓ/g FET = 0.40 min FET_{Vg} = 19.4 x 10^3 ℓ/g	RT = 0.47 min $^{50\%}V_g$ = 22.7 x 10^3 ℓ/g FET = 0.25 min FET_{Vg} = 12.1 x 10^3 ℓ/g
182	RT = 0.26 min $^{50\%}V_g$ = 12.6 x 10^3 ℓ/g FET = 0.10 min FET_{Vg} = 4.84 x 10^3 ℓ/g	RT = 0.33 min $^{50\%}V_g$ = 16.0 x 10^3 ℓ/g FET = 0.15 min FET_{Vg} = 7.26 x 10^3 ℓ/g	RT = 0.46 min $^{50\%}V_g$ = 22.3 x 10^3 ℓ/g FET = 0.35 min FET_{Vg} = 16.9 x 10^3 ℓ/g	RT = 2.67 min $^{50\%}V_g$ = 129 x 10^3 ℓ/g FET = 2.0 min FET_{Vg} = 96.8 x 10^3 ℓ/g	RT = 1.12 min $^{50\%}V_g$ = 54.2 x 10^3 ℓ/g FET = 0.80 min FET_{Vg} = 38.7 x 10^3 ℓ/g
150	RT = 0.50 min $^{50\%}V_g$ = 24.2 x 10^3 ℓ/g FET = 0.30 min FET_{Vg} = 14.5 x 10^3 ℓ/g	RT = 0.68 min $^{50\%}V_g$ = 32.9 x 10^3 ℓ/g FET = 0.40 min FET_{Vg} = 19.4 x 10^3 ℓ/g	RT = 1.00 min $^{50\%}V_g$ = 48.4 x 10^3 ℓ/g FET = 0.8 min FET_{Vg} = 38.7 x 10^3 ℓ/g	RT = 10.33 min $^{50\%}V_g$ = 500 x 10^3 ℓ/g FET = 8.45 min FET_{Vg} = 409 x 10^3 ℓ/g	RT = 3.23 min $^{50\%}V_g$ = 156 x 10^3 ℓ/g FET = 2.60 min FET_{Vg} = 126 x 10^3 ℓ/g
100	RT = 2.11 min $^{50\%}V_g$ = 102 x 10^3 ℓ/g FET = 1.6 min FET_{Vg} = 77.4 x 10^3 ℓ/g	RT = 3.49 min $^{50\%}V_g$ = 169 x 10^3 ℓ/g FET = 2.9 min FET_{Vg} = 140 x 10^3 ℓ/g	RT = 6.35 min $^{50\%}V_g$ = 307 x 10^3 ℓ/g FET = 5.4 min FET_{Vg} = 261 x 10^3 ℓ/g	RT = 150 min $^{50\%}V_g$ = 7,260 x 10^3 ℓ/g FET = 125 min FET_{Vg} = 6,050 x 10^3 ℓ/g	RT = 28.6 min $^{50\%}V_g$ = 1,380 x 10^3 ℓ/g FET = 23.5 min FET_{Vg} = 1,140 x 10^3 ℓ/g

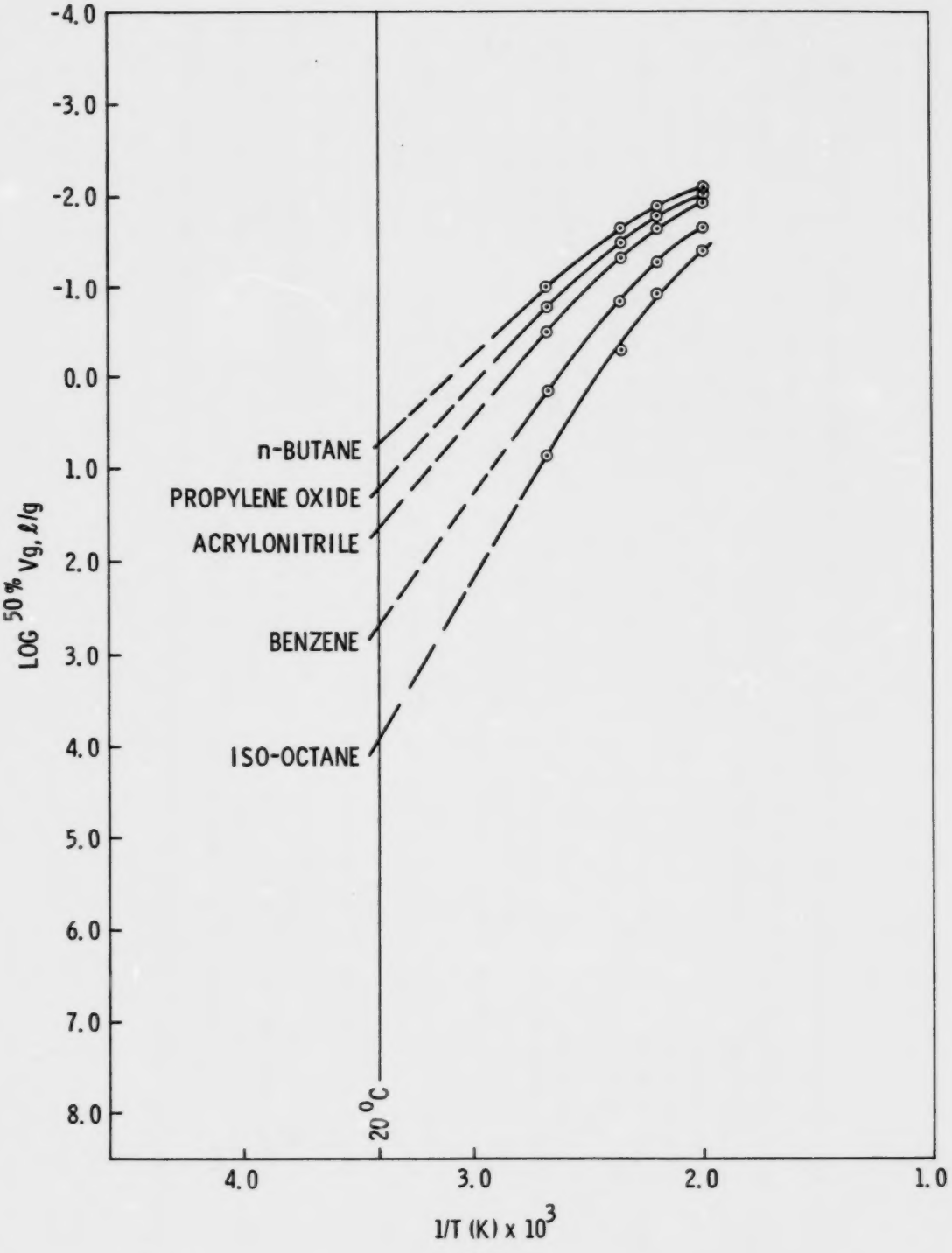

Figure 5. Plot of log $^{50\%}$Vg vs. 1/T for selected test compounds on Porapak R.

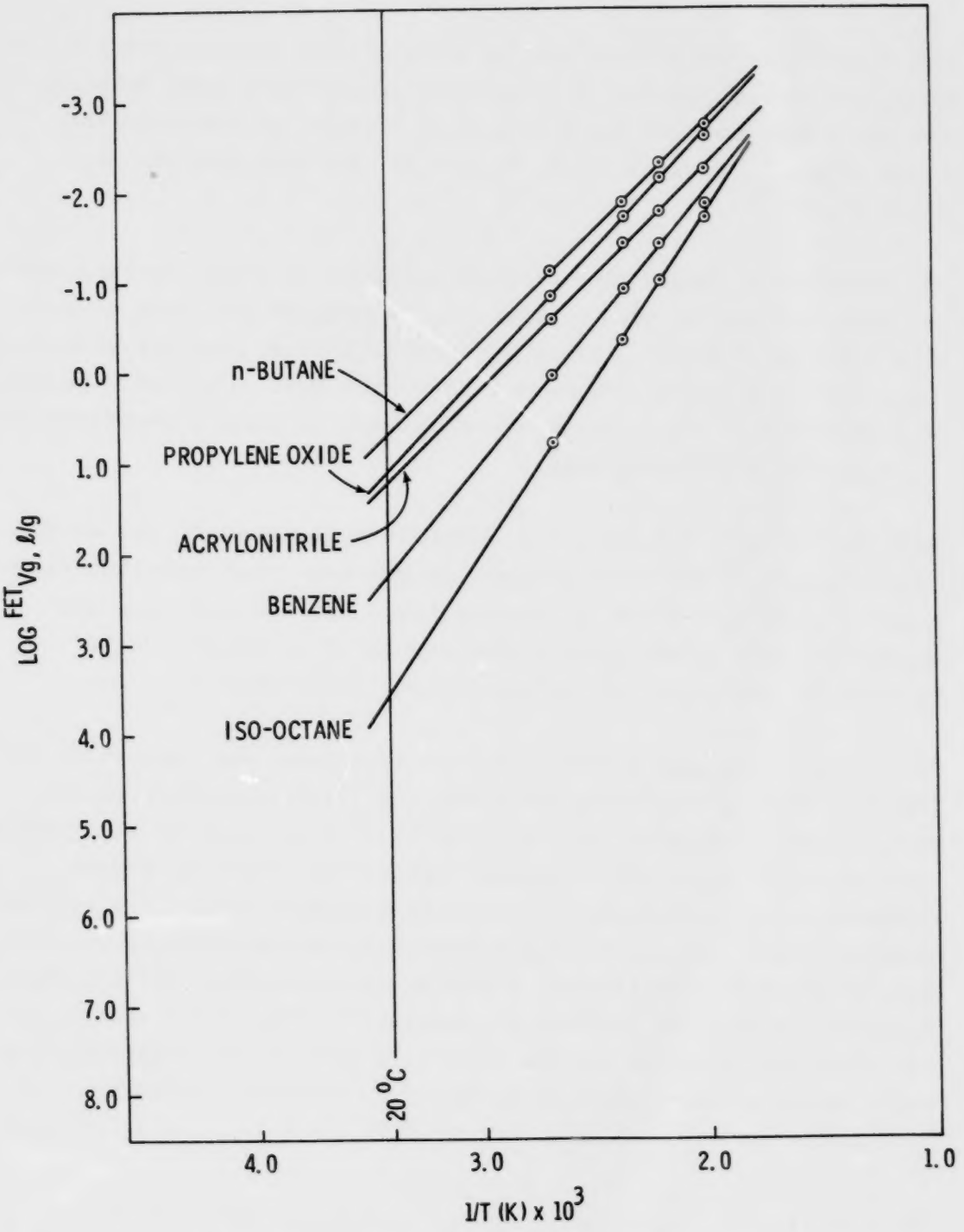

Figure 6. Plot of log ^{FET}Vg vs. 1/T for selected test compounds on Porapak R.

The volumetric capacities for as many of the test matrix and low molecular weight aliphatic compounds as possible were determined for the other sorbent materials in a similar manner from the plots shown in Figures 7, 8, 9, and 10, and are compiled in Table 8.

The volumetric capacities (ℓ/g) determined in these evaluations estimate the volume of air that can be sampled per gram of sorbent materials before sample breakthrough (i.e., before exceeding capacity). This was determined to be the most applicable measure of capacity for our studies since we wish to sample quantitatively (i.e., with no breakthrough).

Methods [4] are available for determining saturation (or weight) capacities, but for this project it was felt that sampling techniques, such as the use of backup tubes and varying sampling volumes, would be an appropriate manner of obtaining valid samples in the event of highly concentrated samples.

As it is a long and arduous task to determine the capacities of a large number of compounds on several sorbent materials by the method just described, it was thought that a means of correlating sorbent capacities with compound properties would be highly desirable. Such a means of correlation would permit the estimation of the $^{FET}Vg_{20°C}$ of any compound on any sorbent by knowing the value of the particular property or properties and how this property is related to sorbent capacity. Then, if a change or addition should occur in the list of compounds of interest, one could state whether the new compound is probably, possibly, or not likely to be quantitatively trapped by a particular sorbent

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[4] Gallant, R. F., J. W. King, P. L. Lewis, and J. F. Piecewicz. Characterization of Sorbent Resins for Use in Environmental Sampling. EPA-600/7-78-054, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978. 151 pp.

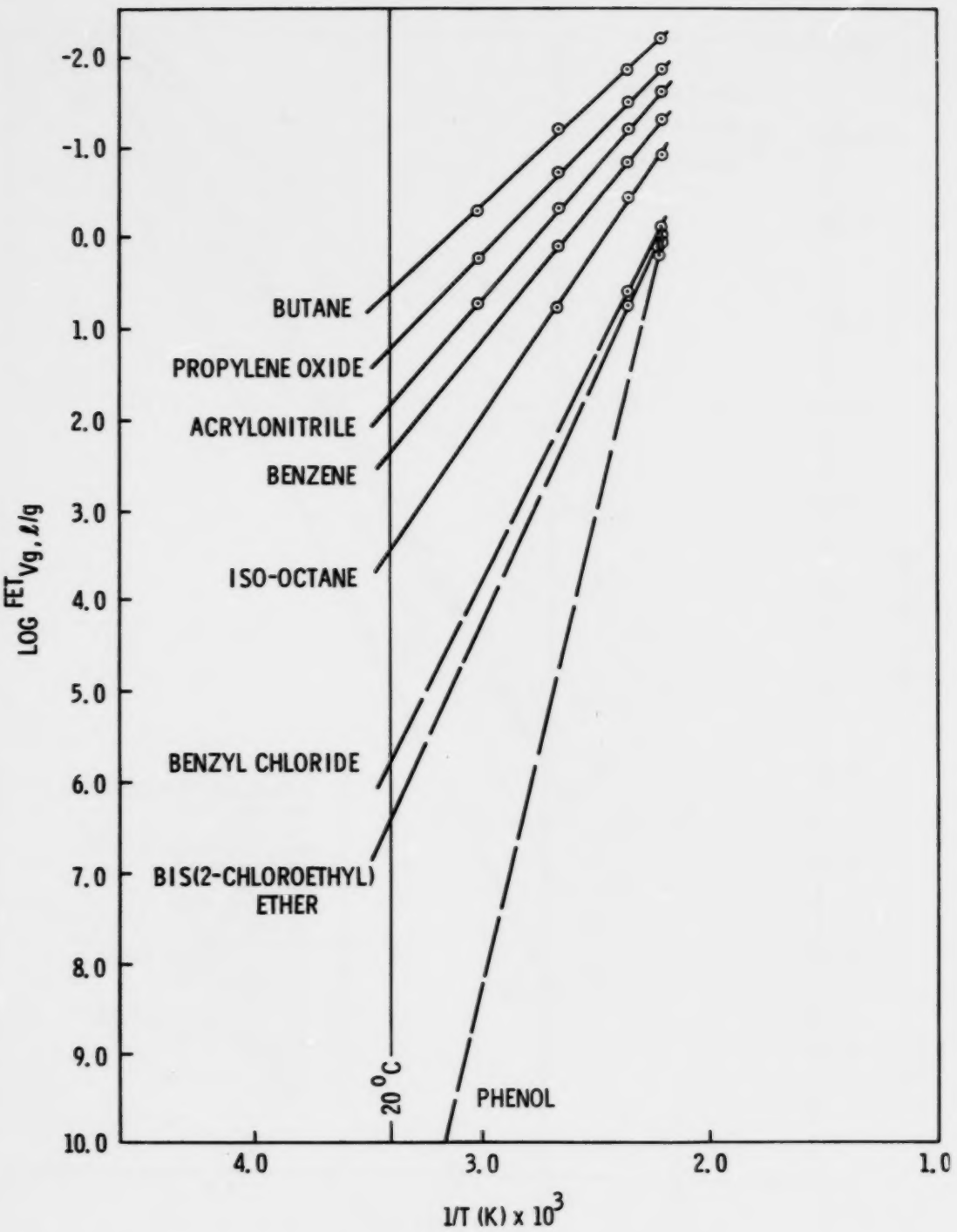

Figure 7. Plot of log ^{FET}Vg vs. 1/T for test compounds on Porapak N.

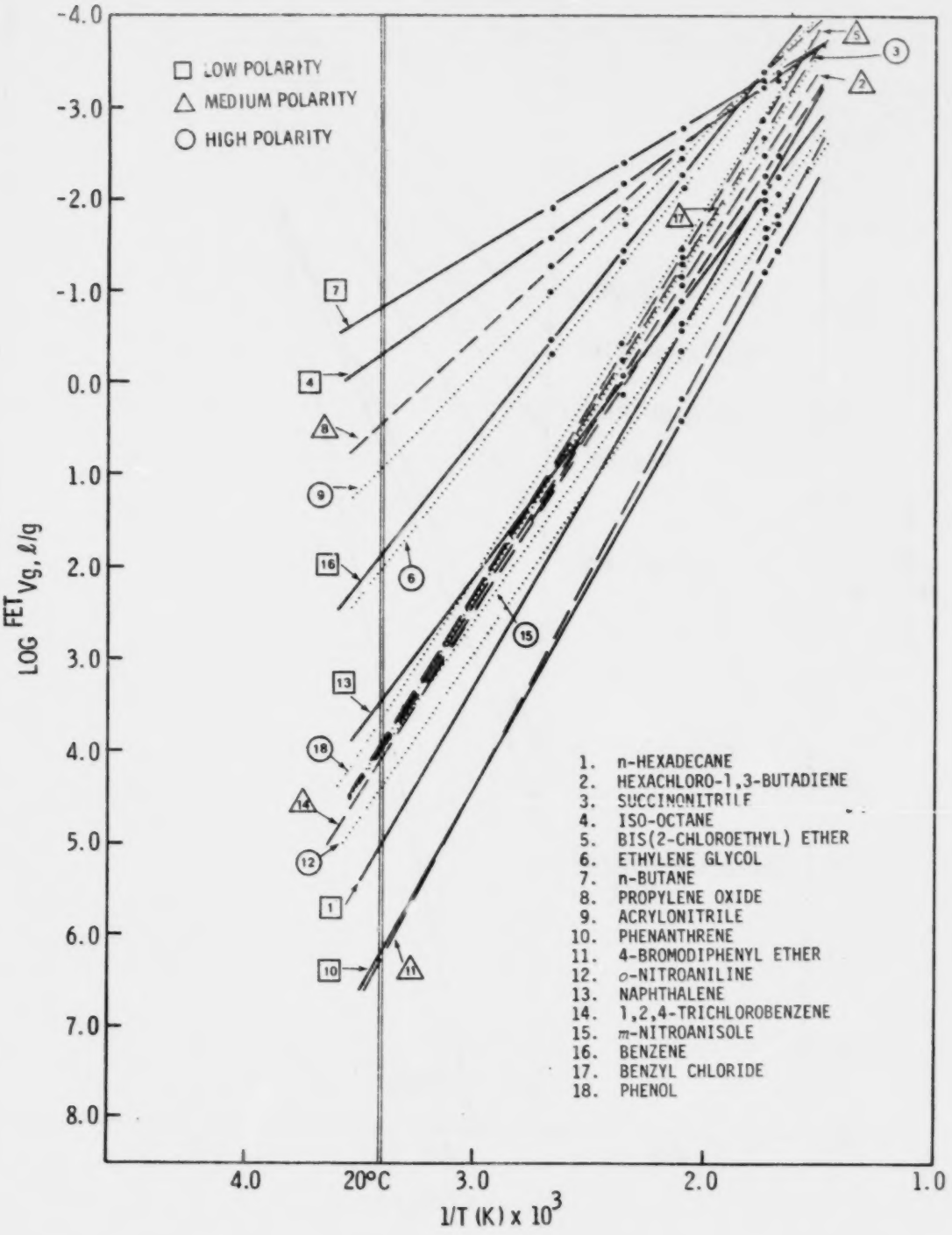

Figure 8. Plot of log ^{FET}Vg vs. 1/T for all test compounds on Tenax-GC.

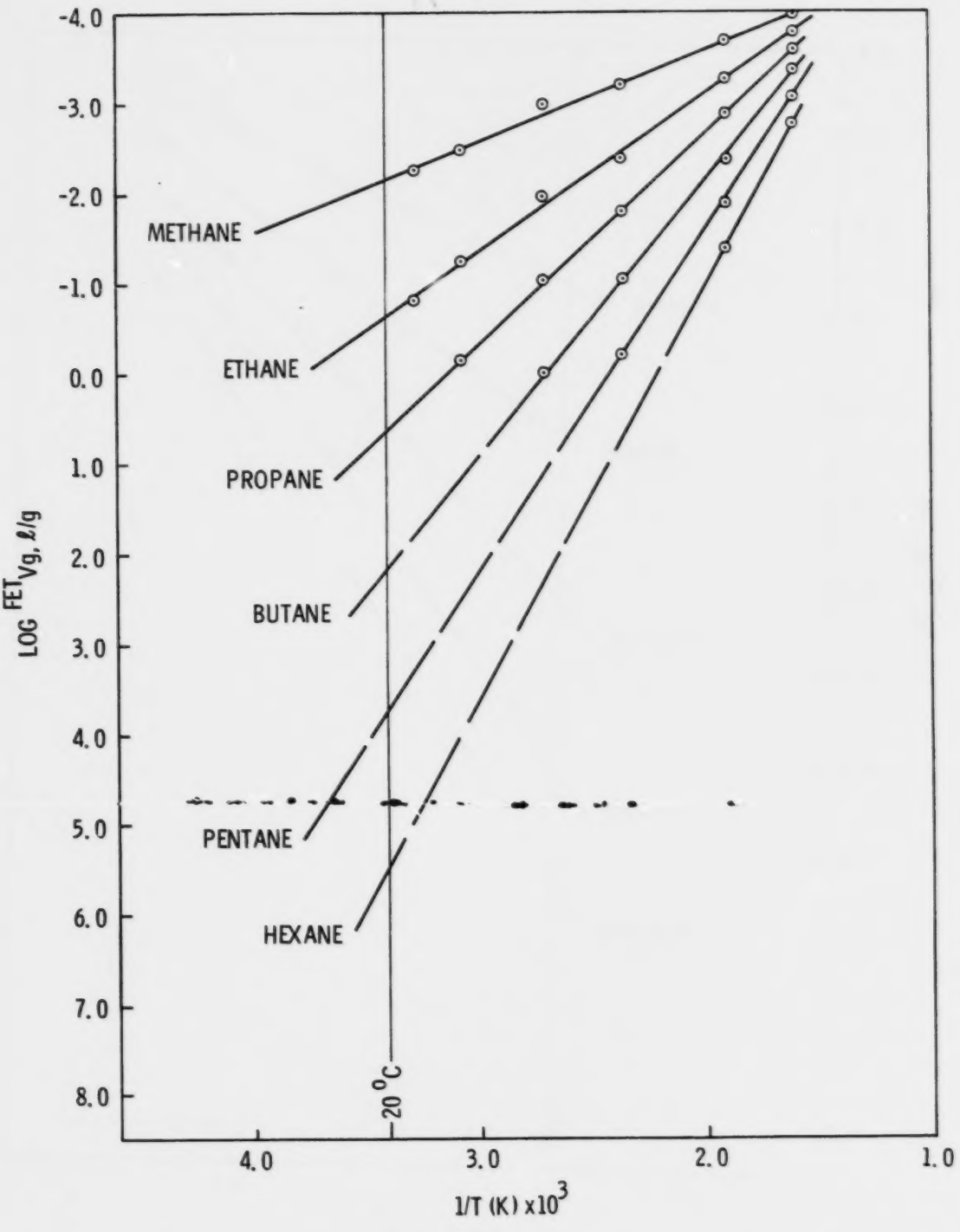

Figure 9. Plot of log ^{FET}Vg vs. 1/T for standard gases on Ambersorb XE-340.

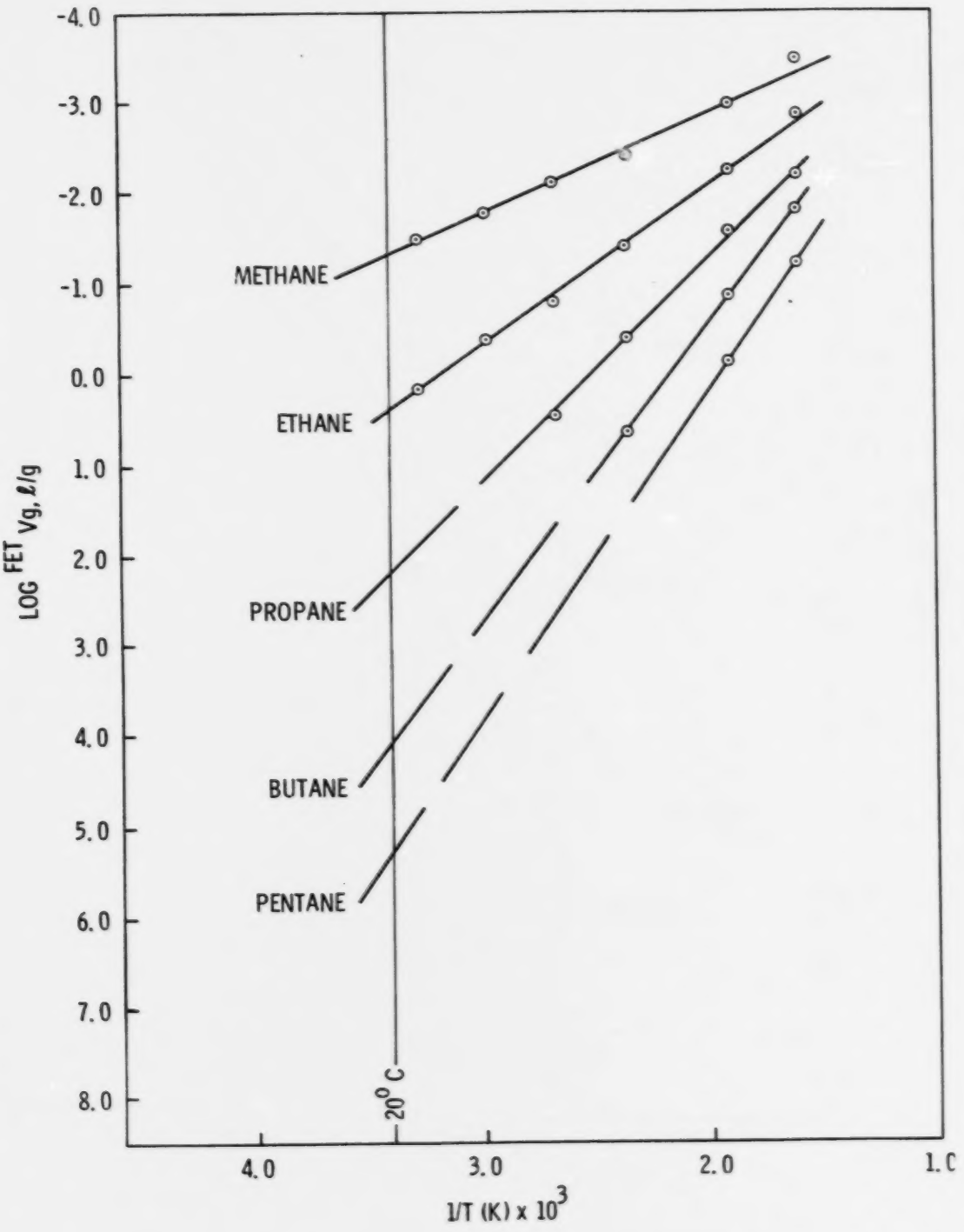

Figure 10. Plot of log ^{FET}Vg vs. 1/T for standard gases on SKC charcoal.

TABLE 8. COMPILATION OF CAPACITY AND SOLUBILITY PARAMETER DATA

Name	δ_m, lit	δ_m, calc	MW	Tenax-GC $FET_{Vg_{20°C}}$, ℓ/g	Tenax-GC log FET_{Vg}	Porapak R $FET_{Vg_{20°C}}$, ℓ/g	Porapak R log FET_{Vg}	Porapak N $FET_{Vg_{20°C}}$, ℓ/g	Porapak N log FET_{Vg}	Ambersorb XE-340 $FET_{Vg_{20°C}}$, ℓ/g	Ambersorb XE-340 log FET_{Vg}	SKC Charcoal $FET_{Vg_{20°C}}$, ℓ/g	SKC Charcoal log FET_{Vg}
Methane	89	-	16.04	-	-	-	-	-	-	0.009	-2.046	0.047	-1.328
Ethane	180	-	30.07	-	-	-	-	-	-	0.229	-0.640	2.40	0.380
Propane	282	282	44.09	-	-	-	-	-	-	5.33	0.727	162	2.210
n-Butane	395	401	58.12	0.16	-0.800	4.93	0.693	3.9	0.591	106	2.025	12×10^4	4.079
n-Pentane	505	519	72.15	-	-	-	-	-	-	7,500	3.875	2×10^5	5.301
Propylene oxide	534	-	58.08	3.14	0.497	12.4	1.092	17.6	1.246	-	-	-	-
Acrylonitrile	557	573	53.06	9.35	0.971	16.8	1.225	69	1.839	-	-	-	-
n-Hexane	629	638	86.17	-	-	-	-	-	-	4×10^5	5.602	-	-
Benzene	719	719	78.11	82	1.914	175	2.244	239	2.378	-	-	-	-
iso-Octane	788	834	114.22	0.532	-0.274	3 550	3.550	2,900	3.462	-	-	-	-
Ethylene glycol	906	-	62.07	120	2.070	-	-	-	-	-	-	-	-
Succinonitrile	-	1,073	80.09	1.04×10^4	4.015	-	-	-	-	-	-	-	-
Phenol	1,176	-	94.11	5,460	3.737	-	-	3×10^{12}[a]	12.477[a]	-	-	-	-
Benzyl chloride[b]	-	1,253	126.58	1.02×10^4	4.007	-	-	6.6×10^5	5.820	-	-	-	-
Naphthalene	1,269	1,410	128.16	3,260	3.513	-	-	-	-	-	-	-	
Bis(2-chloroethyl) ether[b]	1,402	1,402	143.02	1.06×10^4	4.025	-	-	2.8×10^6	6.443	-	-	-	-
o-Nitroaniline	-	1,657	138.12	2.9×10^4	4.460	-	-	-	-	-	-	-	-
m-Nitroanisole	-	1,684	153.13	1.14×10^4	4.058	-	-	-	-	-	-	-	
Phenanthrene	1,747	-	178.22	1.9×10^6	6.282	-	-	-	-	-	-	-	
n-Hexadecane	1,811	1,766	226.43	1.3×10^5	5.113	-	-	-	-	-	-	-	-
1,2,4-Trichloro-benzene[b]	-	2,014	181.46	1.57×10^4	4.195	-	-	-	-	-	-	-	-
4-Bromodiphenyl ether[b]	-	2,616	249.11	2.4×10^6	6.377	-	-	-	-	-	-	-	-
Hexachloro-1,3-butadiene[b]	-	2,783	267.6	1.15×10^4	4.059	-	-	-	-	-	-	-	-

[a] Potentially large experimental error.

[b] Halogenated.

under certain conditions. If sorbent materials were to be used in series for sample collection, one would also have an idea on which sorbent the majority of a certain compound is likely to occur. The general advantage of a means of correlating sorbent capacity and compound properties would be to eliminate the necessity of experimentally determining the capacity of every compound on every sorbent.

The forces that determine the interaction of an organic compound with other materials (neglecting vapor-to-liquid phenomena of nucleation and growth) are: E_d, the dispersion or London forces; E_p, the permanent dipole/dipole forces; and E_h, the hydrogen-bonding forces. These forces are additive and the total interaction energy may be expressed as $E = E_d + E_p + E_h$. Dividing both sides by the nuclear volume of the material, one obtains:

$$E/V = \frac{E_d + E_p + E_h}{V} \qquad (1)$$

since

$$\delta = \left(\frac{E}{V}\right)^{1/2} \qquad (2)$$

where δ = the solubility parameter

then

$$\delta = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (3)$$

The solubility parameter has been well described in the literature [5].

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[5] Burrell, H., and B. Immergut. Solubility Parameter Values. In: Polymer Handbook, J. Brandup and E. H. Immergut, eds. Interscience Publishers, New York, New York, 1966. pp. IV-341 - IV-368.

Many experimental methods exist to determine δ for a compound, and many more methods exist for estimating δ from compound properties such as surface tension. A very useful method of estimating δ from the structural formula, density, and molecular weight of a compound has been developed by Small [6].

Accordingly, δ_d, δ_p, δ_h, and δ were examined for a number of compounds. However, no correlation of the separate or total forces with the $^{FET}Vg_{20°C}$ was found. One would expect a correlation with the dominant force factor, if one should exist, and a correlation with δ would seem even more reasonable. However, of two compounds with similar δ values, the compound with the higher molecular weight (or size) would be expected to have a larger $^{FET}Vg_{20°C}$ on a given sorbent due to its lesser volatility. Therefore, various molecular weight adjustments of δ were tried. The simple expedient of multiplying δ by the molecular weight gives a relative size dependent factor, $\delta_m = \delta \cdot MW$, which has the units of $(g^2 \cdot cal)^{1/2} / (cm^3 \cdot mole)$. The molecular-weight-modified solubility parameters (δ_m) for the test matrix and low molecular weight aliphatic compounds, both from literature and calculated [4] solubility parameter values, are given in Table 8 along with sorbent capacity data. The data for δ_m are plotted versus the log $^{FET}Vg_{20°C}$ for SKC charcoal, Ambersorb XE-340, Porapak N, and Tenax-GC in Figure 11 and for Porapaks R and N in Figure 12. The correlation coefficients for the "best" lines in these figures are given in Table 9.

Note that the most divergent results occur for a few halogenated compounds on Tenax-GC. Unusual behavior of such compounds on Tenax-GC had been noted previously during capacity studies. It was postulated that some sort of solubility effect was possibly occuring since Tenax-GC has a solubility parameter similar to

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[6] Small, P. A. Some Factors Affecting the Solubility of Polymers. Journal of Applied Chemistry, 3(2):71-70, 1953.

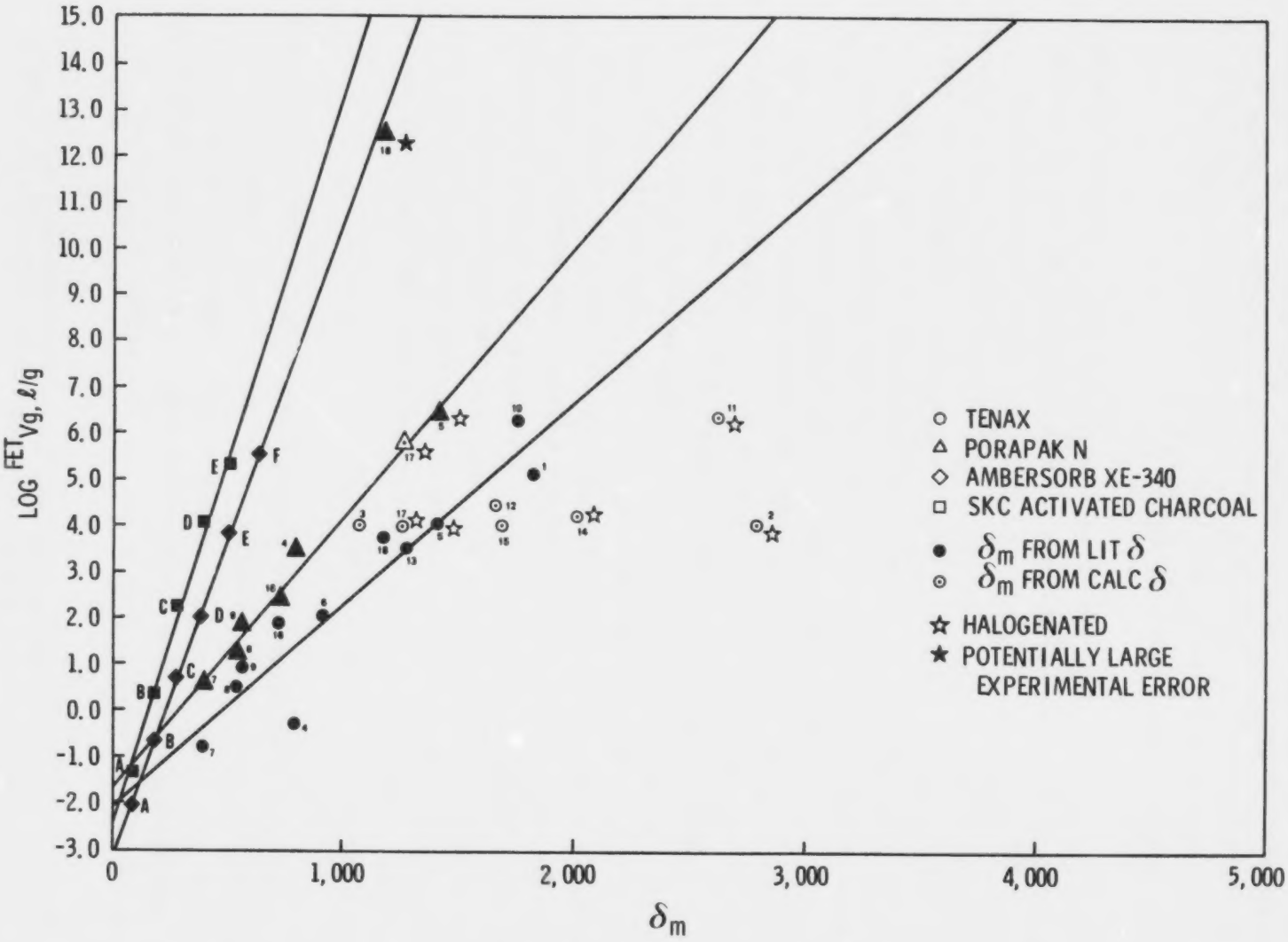


Figure 11. Correlation of δ_m and log $^{FET}Vg_{20°C}$ for test compounds on sorbent materials.

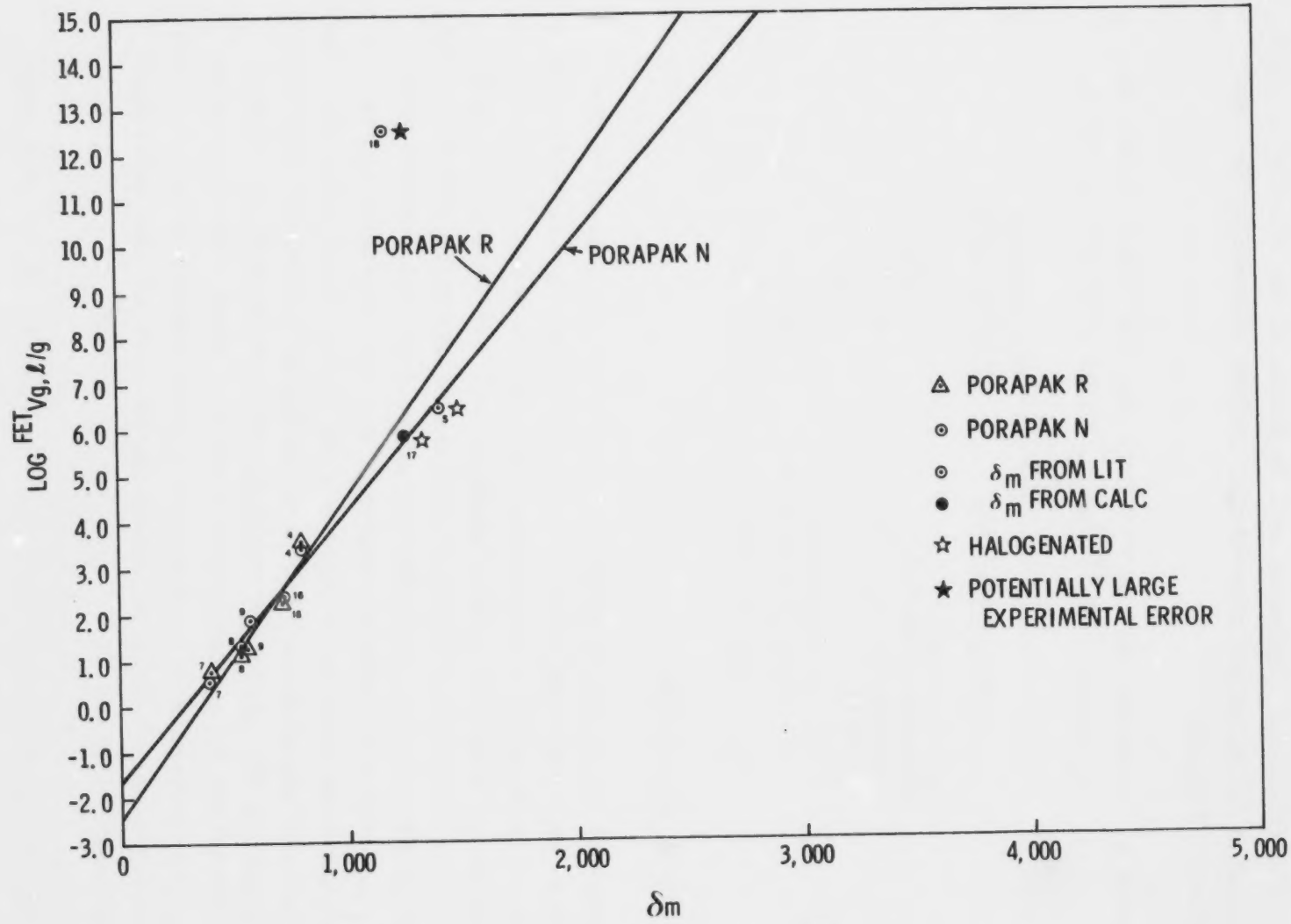


Figure 12. Correlation of δ_m and log $^{FET}V_g$ for selected test compounds on sorbent materials.

that of halogenated compounds and is known to be soluble in such halogenated solvents as chloroform, carbon tetrachloride, and methylene chloride.

TABLE 9. CORRELATION COEFFICIENTS FOR THE "BEST" LINES OF δ_m VERSUS LOG $^{FET}Vg_{20°C}$ PLOTS (FIGURES 11 AND 12)

Sorbent material	Correlation coefficient
SKC charcoal	0.996
Ambersorb XE-340	0.999
Porapak N	0.993
Porapak R	0.944
Tenax-GC	0.806
Tenax-GC (excluding halogenated compounds)	0.916

Desorption Properties

A number of experiments were also conducted to determine how amenable the selected sorbents are to thermal desorption. These experiments were of a preliminary nature since the analytical system to be used for sample analyses was not completely developed. Also, the desorption properties of specific compounds for analysis depend upon the compound as well as the sorbent material, and the test matrix compounds are not necessarily the compounds that will be of interest in future field studies. The preliminary experiments that were conducted attempted to evaluate the sorbents for efficient compound desorption and extraneous background due to contamination and/or sorbent characteristics. Further experiments with the carcinogenic compounds of interest for field sampling will be conducted as part of the analytical development of Phase II.

For the desorption efficiency experiments, 15 cm (6 in.) long, 0.6 cm (1/4 in.) O.D., 4 mm I.D. glass sampling tubes were packed

with the sorbent materials listed in Table 10 and evaluated on the desorption/analytical system depicted in Figure 13. Note that the Chromalytics Concentrator oven contains a six-port, two-position valve, which is sketched in Figure 14. This valve offers the alternative of direct syringe injection of a standard or thermal desorption of a sampling tube. Standards were prepared with a 1,000 μg/mℓ concentration in acetone and stored in septum-capped vials. Chromatographic conditions were established by direct injections of standards using a 2.1 m (7 ft) long, 0.6 cm (1/4 in.) O.D., 2 mm I.D. glass analytical column containing 1.125 g of Tenax, which was conditioned at 320°C overnight. For statistical determination, replicate, direct injections (∿1 μℓ) were made of each standard under the chosen chromatographic conditions and the areas of the peaks integrated by a Hewlett-Packard Model 3354 Lab Automation System. Sampling tubes were placed in the desorption chamber, conditioned briefly (∿30 min), and quickly investigated for background under the desorption/chromatographic conditions to be used. Injections (∿1 μℓ) of the prepared standards were made onto the far ends (i.e., farthest from the analytical column) of the sampling tubes, with subsequent thermal desorption into the analytical column for chromatography and peak integration. Desorption efficiencies were determined in the following manner:

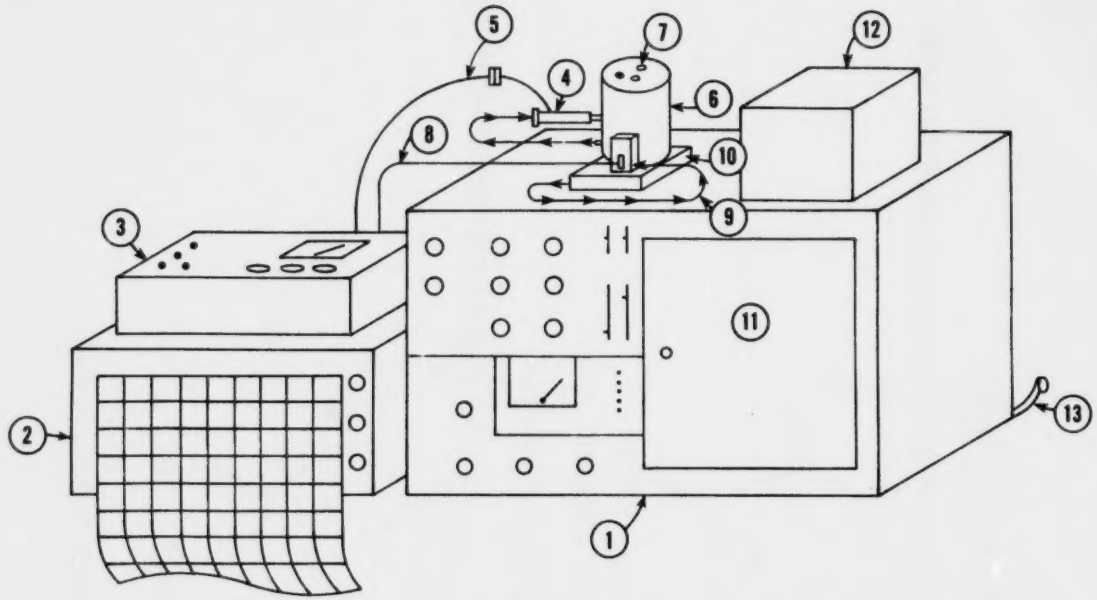
$$\text{Desorption Efficiency} = \frac{\text{(Area of peak from sampling tube desorption)}}{\text{(Average areas/μℓ of peaks from standard injections)}} \times \frac{100}{\text{[Amount (μℓ) injected onto sampling tube]}} \quad (4)$$

In order to establish a median and a range, the desorption efficiency was determined at least three times for each compound on each sorbent.

Since these experiments were preliminary only a few of the test matrix compounds were used in the evaluation of the desorption

TABLE 10. SAMPLING TUBE DATA (ALL SORBENT-FILLED TUBES HAVE GLASS WOOL PLUGS)

Sorbent material	Tube No.	Soxhlet extraction information	Amount of sorbent material, g	Manufacturer's temperature limit, °C	Conditioning temperature, °C	Desorption temperature, °C
Tenax (60/80 mesh)	38	None	0.1218	400	325	300
Tenax (60/80 mesh)	7	Overnight with MeOH	0.1507	400	325	300
Tenax (60/80 mesh)	33	Overnight with each MeOH, EtOAc and pentane	0.1399	400	325	300
Porapak R (50/80 mesh)	26	None	0.2604	250	175 and 240	170
Porapak R (50/80 mesh)	15	Overnight with MeOH	0.2805	250	175 and 240	170
Porapak N (50/80 mesh)	40	None	0.3735	190	175	170
Porapak N (50/80 mesh)	30	Overnight with MeOH	0.3386	190	175	170
SKC activated charcoal	34	None	0.4165	-	325	300
SKC activated charcoal	27	None	0.5176	-	320	300
SKC activated charcoal	17	None	0.5507	-	320	300
Ambersorb XE-340	41	None	0.6114	-	320	300
Ambersorb XE-340	43	None	0.5234	-	320	300
Ambersorb XE-340	839	None	0.7179	-	325	300
Ambersorb XE-340	847	Overnight with each MeOH and distilled H_2O	0.7201	-	325	300



① 5710A HEWLETT-PACKARD GAS CHROMATOGRAPH
② 7132A HEWLETT-PACKARD CHART RECORDER
③ CHROMALYTICS THERMAL CONTROLLER TO 1047 CONCENTRATOR SYSTEM
④ CHROMALYTICS TUBE DESORPTION CHAMBER TO 1047 CONCENTRATOR SYSTEM
⑤ THERMOCOUPLE CONNECTION FROM DESORPTION CHAMBER TO THERMAL CONTROLLER
⑥ CHROMALYTICS OVEN WITH VALVE TO 1047 CONCENTRATOR SYSTEM (200 ^{0}C)
⑦ INJECTION PORT FOR DIRECT INJECTIONS
⑧ THERMOCOUPLE CONNECTION FROM OVEN TO THERMAL CONTROLLER
⑨ NITROGEN CARRIER GAS(30 mℓ/min) INTO CHROMALYTICS VALVE
⑩ CHROMALYTICS OVEN/GC INJECTION PORT (250 ^{0}C) CONNECTION
⑪ GC OVEN CONTAINING 2.1 m LONG, 0.6 cm O.D., GLASS COLUMN WITH 1.125 g OF TENAX (60/80 MESH)
⑫ FLAME IONIZATION DETECTOR (350 ^{0}C)
⑬ GC CABLE TO CENTRAL 3554 HEWLETT-PACKARD COMPUTER SYSTEM

Figure 13. Desorption/analytical system used in desorption efficiency evaluations.

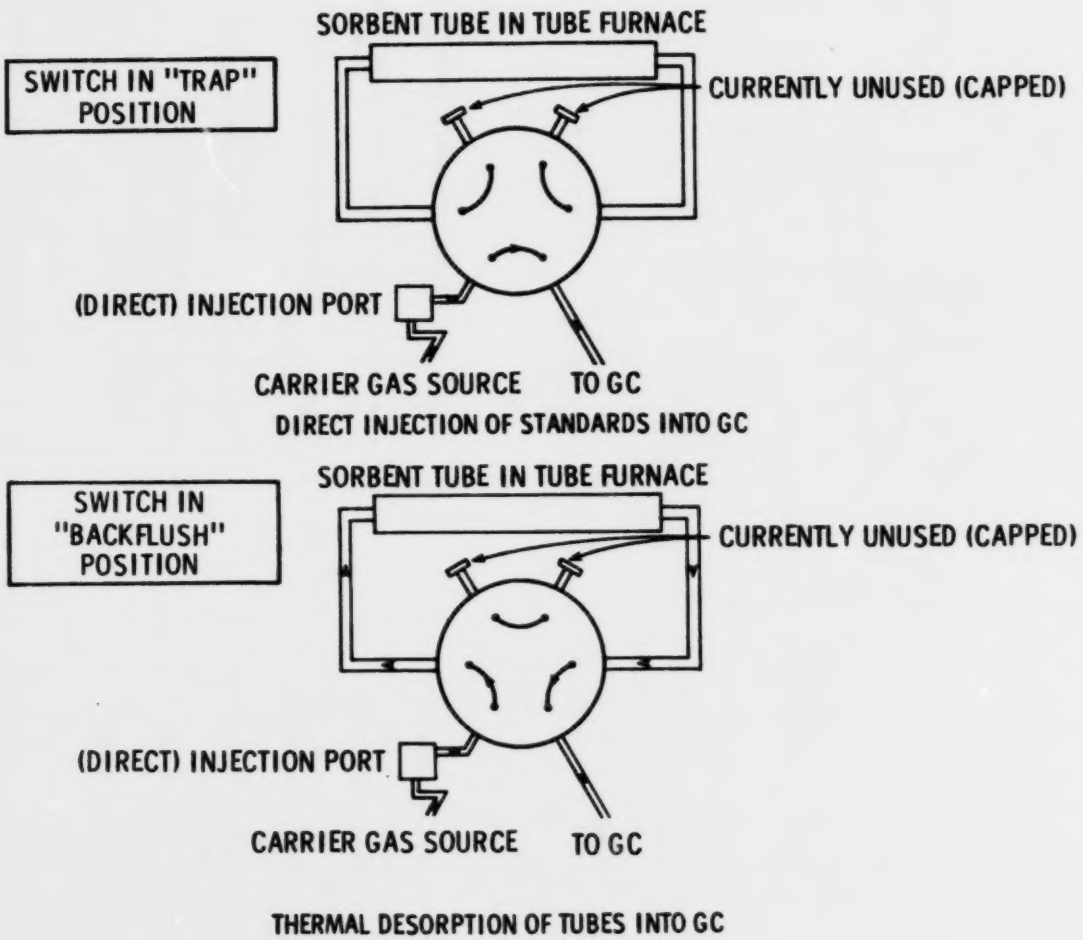


Figure 14. Diagram of six-port, two-position valve within the Chromalytics oven.

properties of the sorbents. However, by relating desorption efficiency to retention time data found previously (for capacity studies using 0.9 m long, 2 mm I.D., 0.6 cm O.D. glass columns filled with the sorbents) at or near desorption temperatures, an idea of the types of compounds that are readily thermally desorbed from the selected sorbents may be obtained. Table 11 gives the chromatographic conditions and raw data for the determinations with the porous polymer type sorbent materials, while Table 12 presents retention time data along with experimentally determined desorption efficiencies. Note that several values are above 100% efficiency. This may be due to either background contributions to peak areas (especially for Porapaks), or slight differences in peak shapes between direct injections and tube desorptions resulting in different peak areas. In relationship to the indicated retention times, the desorption efficiency data suggest potentially easy quantitative desorption of compounds with retention times (Table 12) of less than a few ($\sim$15) minutes. This, in turn, indicates that Tenax is probably very amenable to the quantitative thermal desorption of all 18 test compounds (assuming no decomposition problems) and potentially of other, less volatile substances. Compounds with retention times (Table 12) of greater than about 15 minutes, such as benzyl chloride on Porapak N, may also be amenable to quantitative thermal desorption if the desorption period is prolonged and the sample is reconcentrated in a capillary trap or on the head of the analytical column.

Unfortunately, this experimental procedure, which worked quite adequately for the porous polymers, proved not to be amenable to the evaluation of desorption efficiencies of the carbonaceous adsorbents. Much broader peaks resulted from the thermal desorption of sampling tubes compared with those peaks produced by standard injection. This was due to the longer retention times for thermally desorbed samples that resulted from their having to pass through the sorbent tube as well as the analytical column.

TABLE 11. CHROMATOGRAPHIC CONDITIONS AND RAW DATA FOR THE DETERMINATION OF DESORPTION EFFICIENCIES

Compound	Chromatographic conditions	Average RT of standards, min	Average area for standard, counts/µℓ	Sampling tube	Cond. temp., °C	Des. temp., °C	Trial	Amt. of std., µℓ	RT, min	Area, counts	Desorption efficiency, %
iso-Octane	Temperature programmed from 50°C @ 2°C/min for 10 min then @ 32°C/min to a final 250°C temperature and held there for 8 min	2.98	15,694	Tenax #7	300	300	1	1.10	3.59	16,805	97
							2	1.15	3.35	20,929	116
							3	1.10	2.93	17,984	104
		3.14	(Carrier-He)[a] 9,376	Porapak R #26	235	150	1	1.05	3.95	11,075	112
							2	1.15	3.73	11,288	105
							3	1.09	4.05	10,805	106
		3.32	14,713	Porapak N #30	175	150	1	1.15	3.74	19,062	113
							2	1.15	4.07	18,906	112
							3	1.13	4.07	18,759	113
Naphthalene	Temperature programmed from 150°C to 250°C @ 8°C/min and held at the final temperature for 4 min	10.85	346,086	Tenax #7	300	300	1	1.10	10.88	368,397	97
							2	1.10	10.89	355,569	93
							3	1.00	10.89	334,466	97
							4	1.00	10.88	327,426	95
		11.33	350,729	Porapak R[b] #15	235	220	1	1.19	>30	-	-[b]
		11.30	341,814	Porapak N[b]	175	150	1	1.16	>30	-	-[b]
Phenanthrene	Temperature programmed from 200°C to 300°C @ 32°C/min and held 4 min	7.72	205,658	Tenax #7	300	300	1	0.80	7.85	182,183	111
							2	0.65	8.01	139,996	105
							3	0.80	7.96	181,463	110
n-Hexadecane	Temperature programmed from 200°C to 250°C @ 4°C/min and held @ 250°C for 4 min	9.00[c]	291,098[c]	Tenax #7	300	300	1[c]	1.00	9.25	270,396	95
							2	1.10	9.21	312,449	98
		8.95[c]	292,206[c]				3[c]	1.15	9.11	333,698	99
							4	1.10	9.10	322,293	100

[a] Carrier was nitrogen for all other experiments.

[b] No indication of sample desorption after 30 min at experimental conditions.

[c] Trials 3 and 4 were conducted on a different day from trials 1 and 2 using the same tube (Tenax #7). Slightly different values for average retention time and counts/µℓ were obtained for the standards used in these analyses.

TABLE 12. RETENTION TIME DATA AND DESORPTION EFFICIENCIES AT OR NEAR DESORPTION TEMPERATURE FOR SORBENT MATERIALS

Test compound	δ_m	Retention time, min			
		Porapak N	Porapak R		Tenax
		@ 150°C	@ 150°C	@ 222°C	@ 302°C
n-Butane	395	0.51	0.50	0.17	0.10
Propylene oxide	534	1.03	0.68	0.20	0.11
Acrylonitrile	557	1.93	1.00	0.24	0.08
Benzene	719	4.48	3.23	0.47	0.12
iso-Octane	788	12.1 (113±1%)[a]	10.33 (108±4%)	0.85 (>132%)[b]	0.11 (106±10%)
Ethylene glycol	906	-	-	-	0.11
Succinonitrile	1,073	-	-	-	0.17
Phenol	1,176	-	-	-	0.17
Benzyl chloride	1,253	110	-	-	0.16
Naphthalene	1,269	-[c]	-	-[c]	0.22 (95±2%)
Bis(2-chloroethyl) ether	1,402	165	-	-	0.15
Nitroaniline	1,657	-	-	-	0.41
Nitroanisole	1,684	-	-	-	0.33
Phenanthrene	1,747	-	-	-	1.02 (109±4%)
n-Hexadecane	1,811	-	-	-	0.21 (98±3%)
1,2,4-Trichlorobenzene	2,014	-	-	-	0.20
4-Bromodiphenyl ether	2,616	-	-	-	0.61
Hexachloro-1,3-butadiene	2,783	-	-	-	0.18

[a] Numbers in parentheses are desorption efficiencies.

[b] Significant contribution from sorbent background.

[c] No indication of sample desorption after 30 min at experimental conditions.

The difference in the peak shapes made it impossible to accurately compare peak areas with the standards by this technique. For example, n-butane has a retention time of 0.6 min on a 0.9 m column containing 1.11 g of Ambersorb XE-340 at 300°C, but desorption at the same temperature from a sampling tube containing ∿0.6 g of this adsorbent resulted in a retention time of 1.4 min and an average desorption efficiency of only 76%. Similar results were obtained for n-butane with charcoal-filled sampling tubes. It is uncertain how amenable these carbonaceous sorbents will be to thermal desorption. It is possible that with the sample reconcentrated after a prolonged desorption period, some of the more volatile compounds could be analyzed. However, solvent desorption of these materials may prove to be more desirable.

In addition to desorption efficiencies and retention time data at or near desorption temperature, Table 12 also gives δ_m values for the compounds listed. This table indicates a relationship between these retention times and δ_m, especially for Porapaks R and N. This relationship suggests that δ_m may be used to determine which compounds will be quantitatively desorbed from sorbent materials.

Since a fair correlation has been demonstrated for δ_m and sorbent capacity, and a relationship potentially exists for δ_m and desorption efficiency, then δ_m may be useful in determining which compounds are likely to be quantitatively adsorbed on and subsequently desorbed from a particular sorbent material. A qualitative comparison of δ_m with sorbent capacity and desorption efficiency is given in Table 13. The entries in this table are defined in the key beneath it and are based upon a combination of experimental data, demonstrated correlations, and chemical intuition. The enclosed regions indicate compounds which are probably or possibly quantitatively trapped and are probably or possibly quantitatively desorbed from the sorbent materials indicated. These regions correspond to ranges of δ_m values which are listed in Table 14.

TABLE 13. QUALITATIVE EVALUATION OF TWO SORBENT PROPERTIES COMPARED TO δ_m TO DETERMINE RANGES OF SORBENT UTILITY

Name	δ_m, lit	δ_m, calc	Tenax-GC Trap	Tenax-GC Desorb	Porapak R Trap	Porapak R Desorb	Porapak N Trap	Porapak N Desorb	Ambersorb Trap	Ambersorb Desorb	SKC Charcoal Trap	SKC Charcoal Desorb
Methane	89	–	00	!	00	!	00	!	00	!	00	!
Ethane	180	–	00	!	00	!	00	!	00	!	00	!
Propane	282	282	00	!	00	!	00	!	00	!	✓	!?
n-Butane	395	401	00	!	00	!	00	!	✓	!?	✓	!?
n-Pentane	505	519	00	!	00	!	00	!	✓	!?	✓	!?
Propylene oxide	534	–	00	!	00	!	00	!	✓	!?	✓	!?
Acrylonitrile	557	573	00	!	00	!	00	!	✓	!?	✓	!?
n-Hexane	629	638	00	!	00	!	00	!	✓	!?	✓	X
Benzene	719	719	00	!	✓	!	✓	!	✓	X	✓	X
iso-Octane	788	834	00	!	✓	!	✓	!	✓	X	✓	X
Ethylene glycol	906	–	✓	!	✓	!	✓	!?	✓	X	✓	X
Succinonitrile	–	1,073	✓	!	✓	!?	✓	!?	✓	X	✓	X
Phenol	1,176	–	✓	!	✓	!?	✓	!?	✓	X	✓	X
Benzyl chloride	–	1,253	✓	!	✓	!?	✓	!?	✓	X	✓	X
Naphthalene	1,269	1,410	✓	!	✓	!?	✓	!?	✓	X	✓	X
Bis(2-chloroethyl) ether	1,402	1,402	✓	!	✓	X	✓	X	✓	X	✓	X
o-Nitroaniline	–	1,657	✓	!	✓	X	✓	X	✓	X	✓	X
m-Nitroanisole	–	1,684	✓	!	✓	X	✓	X	✓	X	✓	X
Phenanthrene	1,747	–	✓	!	✓	X	✓	X	✓	X	✓	X
n-Hexadecane	1,811	1,766	✓	!	✓	X	✓	X	✓	X	✓	X
1,2,4-Trichloro-benzene	–	2,014	✓	!	✓	X	✓	X	✓	X	✓	X
4-Bromodiphenyl ether	–	2,616	✓	!	✓	X	✓	X	✓	X	✓	X
Hexachloro-1,3-butadiene	–	2,783	✓	!	✓	X	✓	X	✓	X	✓	X

Key to table:

	Probably	Possibly	Not Likely
Trap Quantitatively	✓	✓?	00 (Vg <480 ℓ/g)
Desorb Quantitatively	!	!?	X

TABLE 14. RANGES OF UTILITY OF SOLID SORBENTS BASED ON δ_m

Sorbent	δ_m (Trap)	to	δ_m (Desorb)
SKC charcoal	∿350	to	∿600
Ambersorb	∿450	to	∿750
Porapak N	∿750	to	∿1,500
Porapak R	∿750	to	∿1,500
Tenax-GC	∿950	to	>2,800

Based on these results a sorbent material may be used to sample most compounds with δ_m values falling within its δ_m range. Alternatively, a sorbent material may be selected for sampling studies with a particular compound which has a δ_m value within the δ_m range of utility of the sorbent. For example, a compound with a δ_m value of 2,000 should probably be sampled using Tenax-GC. A compound with a δ_m value of 1,400 falls within the ranges of utility of Porapak N, Porapak R, and Tenax-GC. Since 1,400 is close to the 1,500 δ_m desorption limit of the Porapaks, Tenax-GC would again be the best sorbent (of these five) to evaluate first for sampling this compound. However, a compound with a δ_m value of 1,000 would probably be easier to sample using one of the Porapaks since this value is near the δ_m trapping limit of Tenax-GC. A problem potentially exists for compounds with δ_m values around 750, since this is the δ_m desorption limit of Ambersorb XE-340 and the δ_m trapping limit of Porapaks R and N. Therefore, for a complex organic sample some overlap exists for the ranges of utility (and the types of compound samples) of Tenax-GC and the Porapaks, but a potential gap exists between the ranges of utility of these polymeric adsorbents and the carbonaceous adsorbents. It should be emphasized that these ranges are only estimates of sorbent utility, and it is likely that some compounds may not adhere to this scheme.

The other area of interest during the evaluation of the thermal desorption properties of the selected sorbent materials was potential extraneous background resulting from contamination and/or sorbent characteristics. Sorbent backgrounds can be composed of a variety of contaminants from a number of different sources. Depending upon their degree and nature, these contaminants can lead to complications during both sample collection and analysis. In order to minimize problems from background contamination, it is best to know as much as possible about what types of contamination can arise, how they usually occur, and how best to minimize all sources of contamination. In this way, complications, such as *in situ* reactions and interference during analysis, can be minimized and possibly avoided.

Generally, all commercial sorbent materials as received from suppliers contain significant levels of background contamination as the result of production, packaging, and/or transportation. Although most of this initial contamination may be removed by solvent (before packing in tubes) and/or thermal (usually after packing in tubes) conditioning, such conditioning may also introduce contaminants. Backgrounds may be introduced from trace impurities in the solvent and the gas stream, and also from decomposition products of the polymer. Obviously, one does not heat a polymer above its temperature limit or extract it in a solubilizing solvent, but some polymeric breakdown can occur under other situations as well. For example, Chromosorb 102 is reported to be stable to 250°C by its manufacturer. However, the experimental data shown in Figures 15 and 16 suggest three possible regions of varying thermal stability [7]. Below 170°C both differential scanning colorimetry (DSC) and thermal gravimetric

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[7] Adams, J., K. Menzies, and P. Levins. Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds. EPA-600/7-77-044, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977. 61 pp.

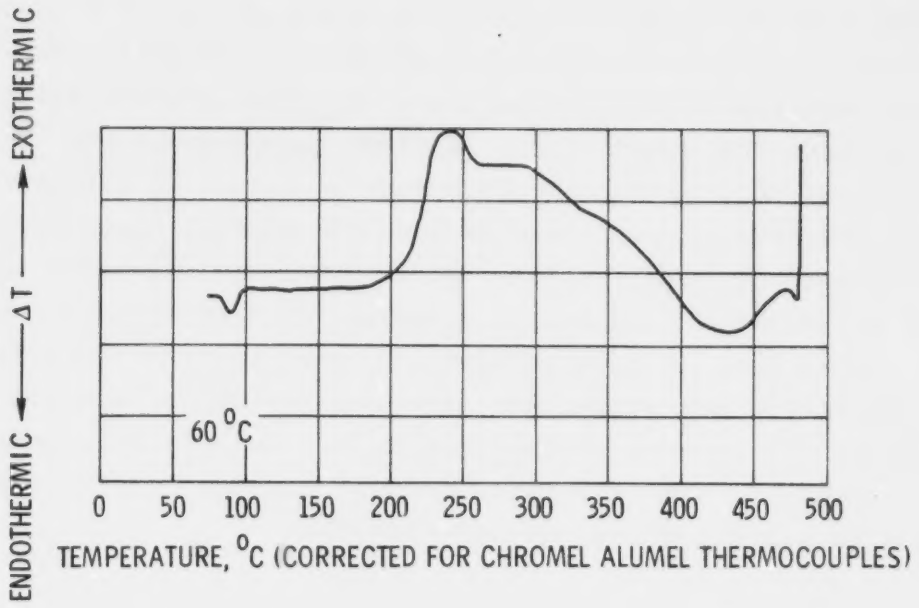

ENDOTHERMIC ← ΔT → EXOTHERMIC
60 °C
0 50 100 150 200 250 300 350 400 450 500
TEMPERATURE, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

Figure 15. Differential scanning calorimetry data for Chromosorb 102 [7].

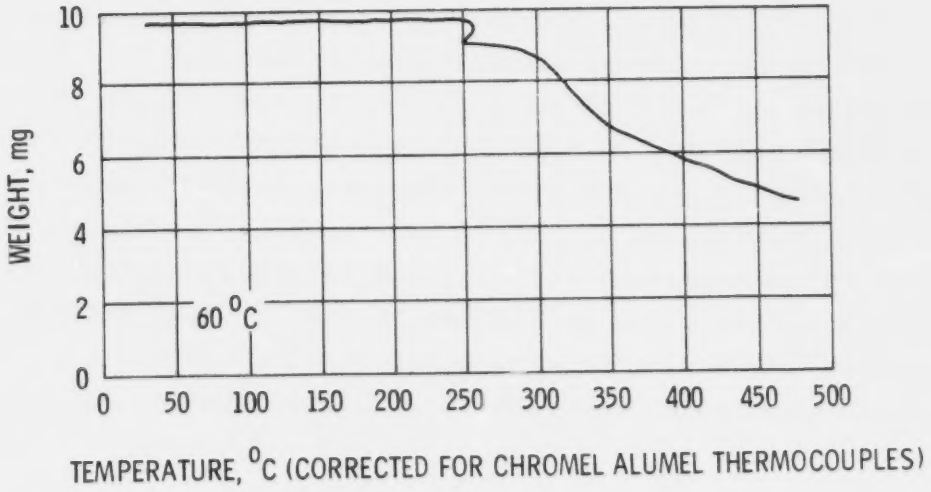


Figure 16. Thermogravimetric analysis data for Chromosorb 102 [7].

analysis (TGA) data indicate a region of excellent thermal stability. Between 170°C and 250°C the DSC data indicate a region of change in thermal properties, perhaps relating to a phase change in the polymer. A change is not indicated by the TGA data until ∿245°C. Above 250°C both the DSC and TGA data definitely indicate the thermal breakdown of Chromosorb 102. Conditioning this sorbent at 240°C might result in a lower background at a 200°C desorption temperature since more of the original background would be removed. However, it could produce a higher background at 200°C due to the increased number of thermal decomposition products that would be produced if the inflection in the DSC traced at ∿200°C indicates the onset of thermal decomposition.

Each sorbent will have thermal properties that are unique and, therefore, conditioning procedures should be validated and optimized for each sorbent material. As a precaution, one should also be aware of the types of compounds each sorbent produces as the result of thermal and/or chemical degradation. Table 15 lists several of the major thermal decomposition products that could be expected from the selected sorbent materials, as well as the chemical compositions and temperature limits of the sorbents. Since the temperature limit of Ambersorb XE-340 was not stated by its manufacturer, a freshly packed 0.9 m long, 0.6 cm O.D., 2 mm I.D. glass column of this sorbent was prepared, conditioned, and analyzed by GC/MS to verify that thermal decomposition was not occurring at the conditioning temperature of 350°C. This column was placed in the GC oven of a Hewlett-Packard Model 5982A GC/MS system and subjected to stepwise temperature increases (50°C intervals) up to 250°C. The effluent from the column was continuously monitored by mass spectrometry (MS) and showed none of the expected thermal decomposition products of the styrene-divinyl benzene polymer. Indeed, the only effluents observed were CO_2, SO_2, argon, and traces of a few low molecular weight aliphatics. Therefore, thermal decomposition of Ambersorb XE-340

does not occur at 350°C, which is above the anticipated operating temperatures.

TABLE 15. EXPECTED THERMAL DECOMPOSITION BEHAVIOR OF SELECTED SORBENT MATERIALS

Sorbent	Chemical composition	Temperature limit, °C	Major thermal decomposition products
Porapak N	N-Vinyl pyrrolidone	190	Vinyl pyrrolidone Pyrrolidone Pyrrilidiene
Porapak R	N-Vinyl pyrrolidone	250	Vinyl pyrrolidone Pyrrolidone Pyrrilidiene
Tenax-GC	2,6-Diphenyl-*p*-phenylene oxide	400	Alkyl benzenes Styrene Benzene Alkyl phenols
Ambersorb XE-340	Carbonized styrene-divinyl benzene	>350	-[a]
SKC activated charcoal	Carbonized organics	>400	-[a]

[a]Major decomposition products not determined.

Once the conditioning procedure for a particular sorbent has been established, care must be taken to prevent additional contamination during subsequent handling. The handling and storing of sampling tubes should be optimized without being unreasonably complicated or expensive. The techniques developed should also ensure the integrity of all samples collected (i.e., no sample loss).

Finally, backgrounds from other sources in the desorption/analytical system should be eliminated or reduced to the greatest extent possible. These can arise not only from the usual sources

of chromatographic background contamination (e.g., column and septum bleed) but also from sources that are unique to the method of desorption and sample introduction. These less obvious difficulties could include dust being introduced into the desorption chamber or fingerprints on the sample tube, depending upon the desorption chamber design. Generally, background contamination introduced by a desorption/analytical system is best minimized by using forethought when designing the system.

A series of experiments was conducted to evaluate the background levels of the materials being studied and possible sources of background within the desorption/analytical system. Sampling tube backgrounds were evaluated by using the desorption/analytical system sketched in Figure 17 and the sampling tubes listed previously in Table 10. Examples of two experimental background chromatograms for a Tenax-GC tube are depicted in Figure 18. Below are some of the findings determined during these evaluations of sorbent backgrounds.

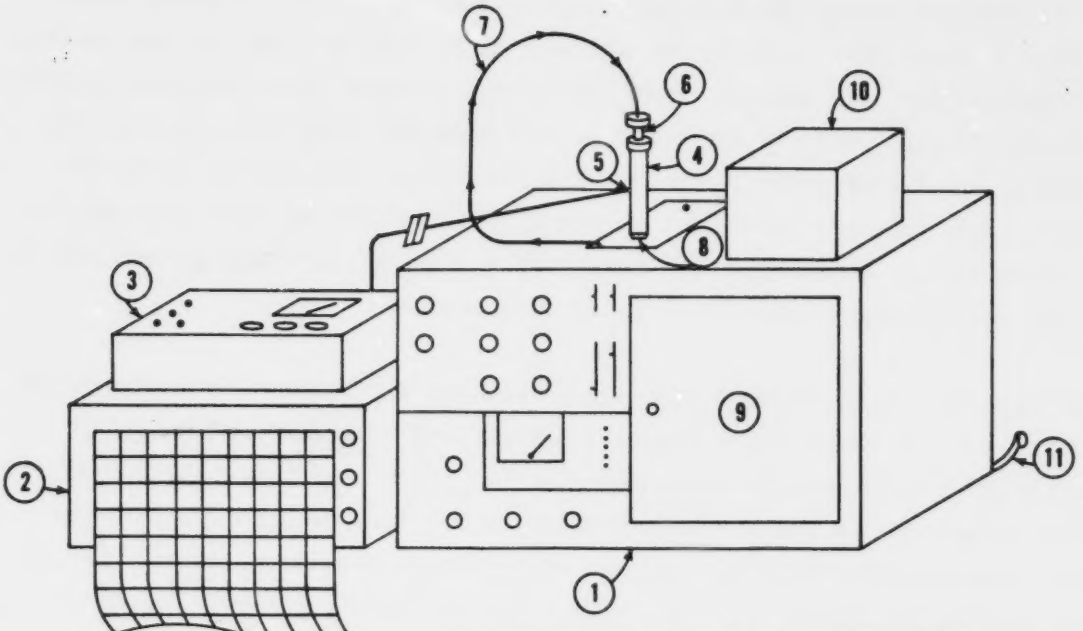
Conditioning--

- No difference was noted between solvent-extracted and non-solvent extracted sorbents (for the sorbents studied and the experimental system used).

- For Porapak R, conditioning at 240°C produced less background upon desorbing at 170°C than with conditioning at 175°C and desorbing at 170°C.

- Thermal conditioning removed a great deal of contamination, most within the first hour.

- After conditioning, the backgrounds of Porapak R and N tubes were above the background of a blank control tube, while the backgrounds of Tenax-GC, Ambersorb XE-340,



① 5710A HEWLETT-PACKARD GAS CHROMATOGRAPH

② 7132A HEWLETT-PACKARD CHART RECORDER

③ CHROMALYTICS THERMAL CONTROLLER TO 1047 CONCENTRATOR SYSTEM

④ CHROMALYTICS TUBE DESORPTION CHAMBER TO 1047 CONCENTRATOR SYSTEM

⑤ THERMOCOUPLE CONNECTION FROM DESORPTION CHAMBER TO THERMAL CONTROLLER

⑥ DESORPTION CHAMBER ENTRANCE AND (O-RING) SEAL

⑦ NITROGEN CARRIER GAS (30 mℓ/min)

⑧ DESORPTION CHAMBER/GC INJECTION PORT (300 ^{0}C) CONNECTION

⑨ GC OVEN (320 ^{0}C) CONTAINING EMPTY 0.9 m LONG, 0.6 cm O.D., 2 mm I.D. GLASS COLUMN

⑩ FLAME IONIZATION DETECTOR (350 ^{0}C)

⑪ GC CABLE TO CENTRAL 3554 HEWLETT-PACKARD COMPUTER SYSTEM

Figure 17. Desorption/analytical system used in tube background evaluations.

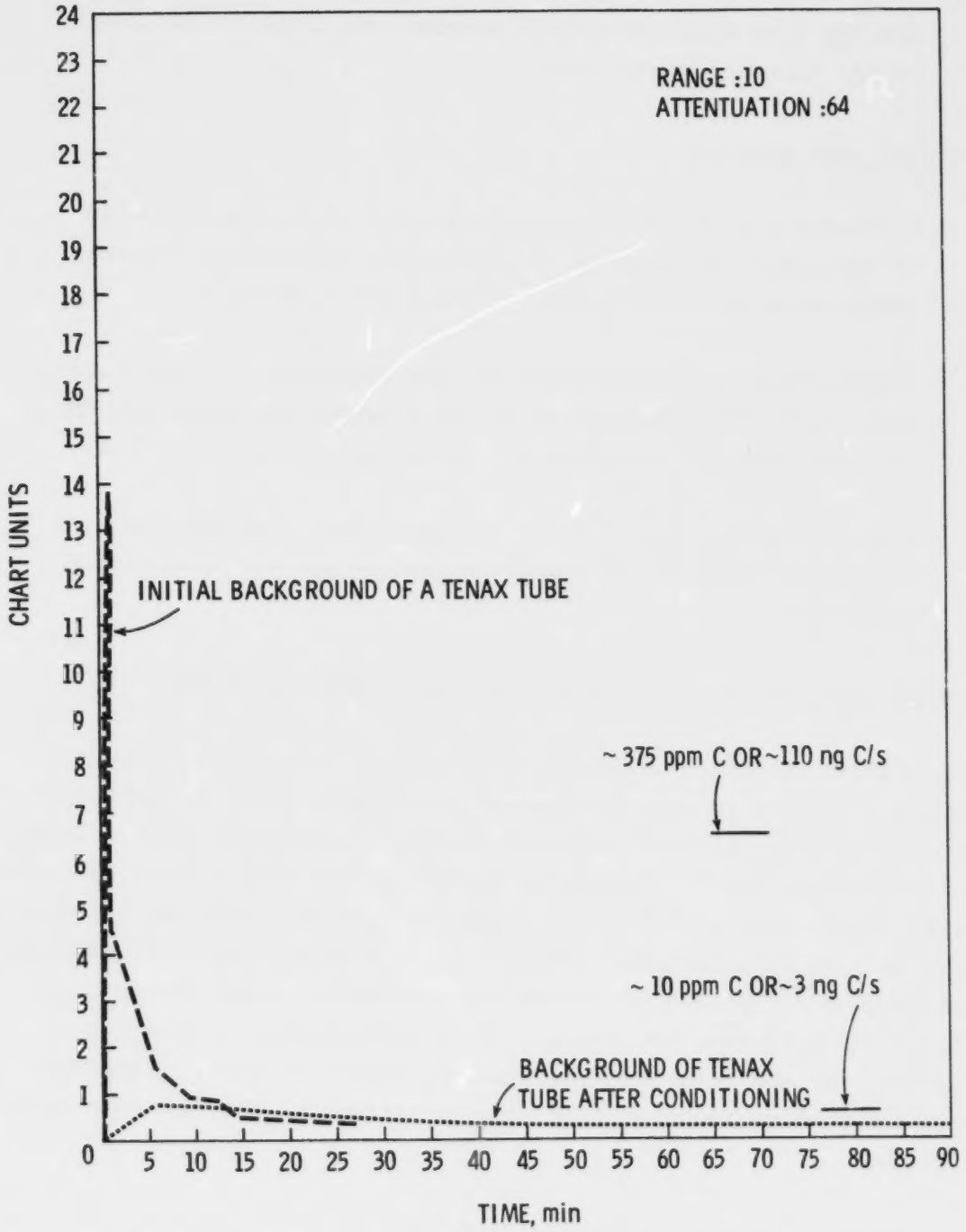

RANGE :10
ATTENTUATION :64
CHART UNITS
INITIAL BACKGROUND OF A TENAX TUBE
~ 375 ppm C OR ~110 ng C/s
~ 10 ppm C OR ~3 ng C/s
BACKGROUND OF TENAX
TUBE AFTER CONDITIONING
TIME, min

Figure 18. Experimental chromatograms of the backgrounds of a Tenax-GC sampling tube before and after conditioning.

and SKC activated charcoal matched the background level of the blank control tube.

Handling and Storage--

- A desorption system designed to eliminate the exterior of the sampling tube from analytical desorption greatly diminishes problems with handling and storage.

- Capping tubes with metal fittings and storing them in culture tubes with Teflon-lined caps seems the best method of tube storage to eliminate extraneous contamination.

- Glass sampling tubes offer a more inert surface than stainless steel with fewer contamination and reactivity problems.

Evaluations of Sampling Tube Pressure Drops and Design

One limitation that automatically applies to any portable air sampling system is the ability of a portable pump to pull air through sorbent-filled sampling tubes at a desired rate. This ability is directly related to the pressure drop across the sampling tube. For a particular pump to pull air through a sampling tube system at a specific rate (0.5 to 3 ℓ/min for this project), the pressure drop across these tubes must be equal to or less than a certain maximum value. This corresponds to the rated capacity of the pump at a particular pressure drop. Sampling tube parameters which affect the magnitude of the pressure drop include:

- Type of sorbent material packing

- Mesh size of sorbent material packing

- Amount of glass wool plug
- Diameter of the tube
- Amount of sorbent material packing

Of the above parameters, the types and amounts of sorbent material packings will be mainly determined by the capacity of these sorbents for atmospheric pollutants under the anticipated sampling conditions. The mesh size of the sorbent materials offers some versatility, but there are limitations to the mesh sizes available. The amount of glass wool used to contain the sorbent material within the tube can be a critical factor in determining the pressure drop, so that care should be taken to ensure that the minimum amount of glass wool is used. In larger diameter tubing, a method of restraining the glass wool plug may be necessary when minimal amounts of glass wool are used. Tapering the ends of the tube or inserting a stainless steel screen are two possible ways to secure the glass wool plugs.

The experimental parameter that offers the most flexibility in determining the pressure drop is the tube diameter. The only restriction on the diameter of the tube is the necessity to achieve rapid and uniform heating of the sorbent bed during the thermal desorption process. This becomes increasingly difficult with increasing sampling tube diameter.

The pressure drops across sampling tubes of various shapes, diameters, and sorbent beddings were measured using a differential pressure gauge. Flow rates were set by using a Brooks Model 5841 thermal mass flow sensor/controller. Owing to the low precision of the differential pressure gauge used in this investigation, the accuracies of the pressure drops measured below 5 psig are questionable, and those measured below 1 psig are only very rough approximations. An example of the type of data generated during

these pressure studies is given in Table 16 and depicted in Figure 19.

These pressure drop studies led to the conclusion that a 10-mm diameter represents a reasonable compromise between the requirement to have the smallest possible diameter for efficient thermal desorption and yet maintain an acceptable pressure drop across sorbent-filled tubes. Two designs, straight and tapered, with 10-mm cross sections were evaluated, taking into account the desirable design features of the miniature collection system. Although the tapered tubes had higher pressure drops than the straight tubes, the difference was not significant. Furthermore, the tapered design offered advantages for the containment of the sorbent since smaller amounts of glass wool can be used with no "blow outs" of sorbent material. If one wished to reduce the required amount of a glass wool even more, stainless steel screens would be easier to place within the tapered tubes than the straight tubes (which would probably have to be scored on their inner surfaces). Finally, lighter, less expensive [0.6 cm (1/4 in.)] fittings can be used with the tapered tubes, which is an important factor in the design and construction of a miniature collector. The specifications for the cartridge design determined to be most desirable are given in Figure 20 along with a sketch of a sampling tube.

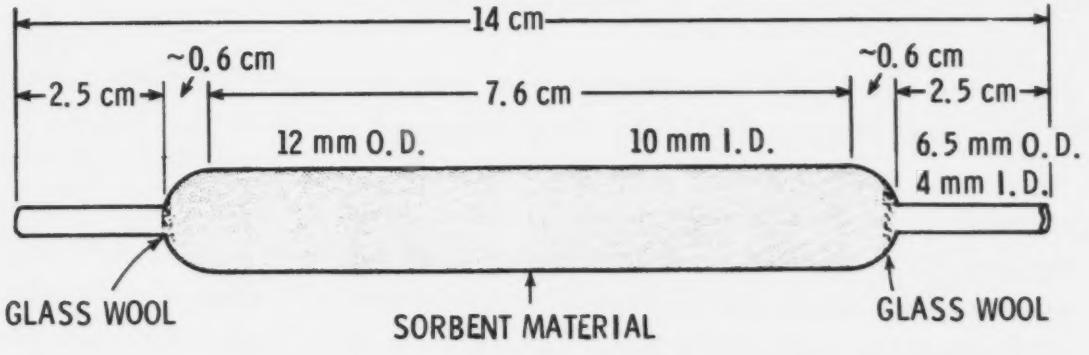


Figure 20. Specifications of selected sampling tube design.

TABLE 16. PRESSURE DROP DATA FOR GLASS SAMPLING TUBES[a]

Flow rate, ℓ/min	Sorbent tube description: Tenax-GC, 60/80 mesh, 0.1953 g, w/34.3 mg glass wool	Tenax-GC, 35/60 mesh, 0.2014 g, w/34.3 mg glass wool	Porapak N, 50/80 mesh, 0.2018 g, w/38.9 mg glass wool	Ambersorb XE-340 (not sieved), 0.1964 g, w/36.1 mg glass wool	Glass tube without sorbent, w/36.2 mg glass wool	Tenax-GC (35/60), Porapak N, and Ambersorb XE-340 in series
	ΔP, psig[b]					
3	23.2	20.3	14.8	3.0	1.1 to 1.2	31.8
2	15.8	12.3	9.0	1.6	0.6	19.9
1	6.4	5.1	3.8	0.4	0.1	8.8
0.5	3.0	2.2	1.6	0.1	-	4.0
0.25	1.5	1.0	0.8	∿0	-	2.0

[a] 15 cm long, 0.6 cm O.D., 4 mm I.D.

[b] 1 psig = 6.9×10^3 pascals (Pa).

Other conditions

Transfer lines only at 3 ℓ/min show ∿0 psig pressure drop.
Inlet pressure: 62 psig; downstream pressure: 9 psig.

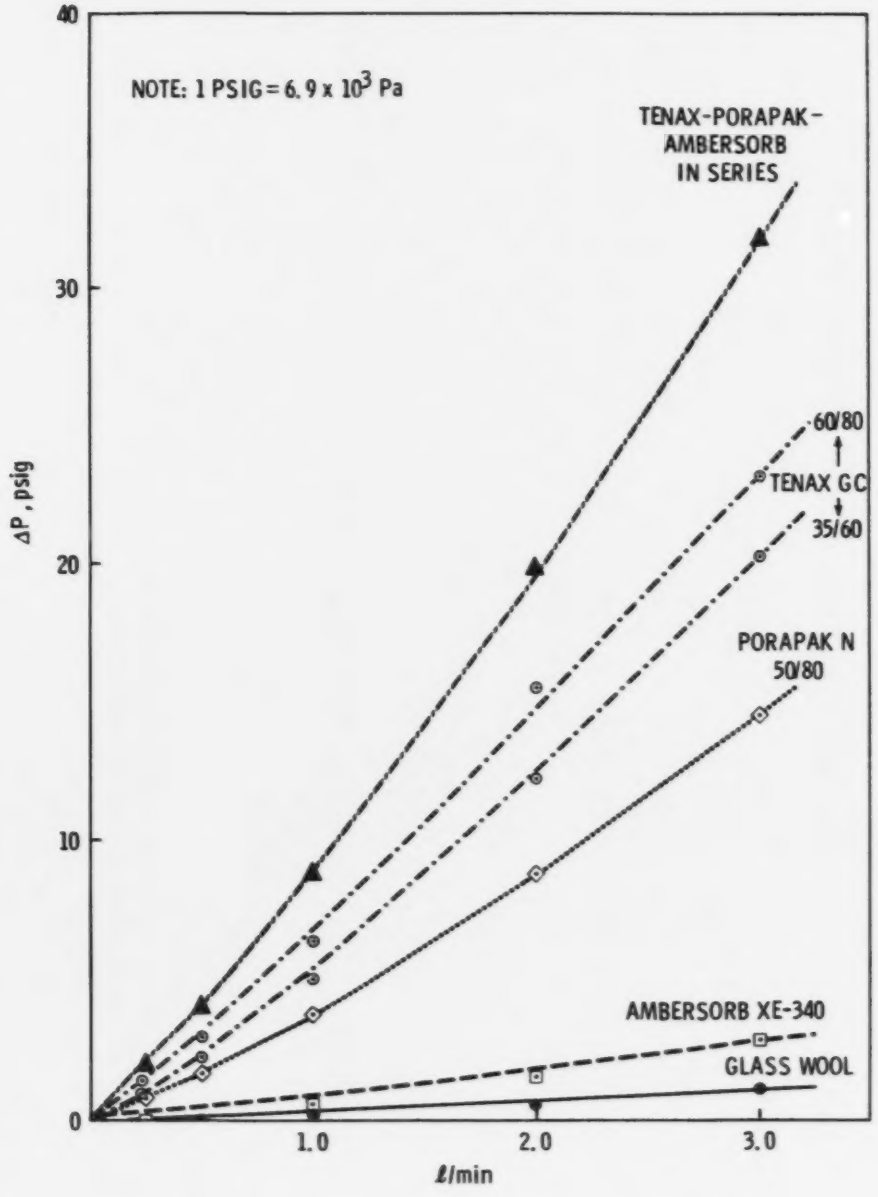


Figure 19. Pressure drops vs. flow rates for 15 cm long, 0.6 cm O.D., 4 mm I.D. glass sampling tubes.

Evaluation of Sorbent Package

Five sorbent materials have been evaluated to determine their basic properties, including special abilities and potential problems.

Table 17 is a compilation of the major sorbent material properties evaluated. Along with the name of the adsorbent are included:

- The manufacturer's stated temperature limit (or >400°C).
- The temperature used for sorbent conditioning.
- The temperature used for sorbent desorption.
- The chemical composition of the polymer.
- Some of the major thermal decomposition products.
- A qualitative description of the background to be expected from the sorbent material.
- The pressure drop across tapered tubes containing 1.0 g of adsorbent at a 3 ℓ/min flow rate.
- A qualitative description of the type of compounds that will potentially be quantitatively trapped by the adsorbent (capacity ≥480 ℓ/g).
- A qualitative description of the type of compounds that will potentially be quantitatively thermally desorbed for analysis.
- The range of utility based on δ_m (described previously in this report).

TABLE 17. ADSORBENT PROPERTIES CHART

Adsorbent	Temp. limit, °C	Cond. temp., °C	Des. temp., °C	Chemical composition	Major thermal decomposition products	Background level	ΔP,[a] psig[b]	Capacity	Desorption	Range of utility, in terms of δ_m
Tenax-GC (35/60 mesh)	400	320	300	2,6-Diphenyl-*p*-phenylene oxide	Alkyl benzene Styrene Benzene Alkyl phenols	GOOD (None detected above system background)	160	Should efficiently trap intermediately (and less) volatile compounds with slightly less affinity for polar compounds.	Very amenable to thermal desorption for intermediately (and all higher) volatile compounds.	∿950->2,800
Porapak R (50/80 mesh)	250	235	150 to 220	N-Vinyl pyrrolidone	Vinyl Pyrrolidone Pyrrolidone Pyrrilidiene	After conditioning at 235°C, background upon desorbing is: POOR @ 220°C (well above system background) FAIR @ 150°C (slightly above system background)	∿1.1[c]	Should efficiently trap intermediately (and less) volatile compounds with slightly greater affinity for polar compounds.	Very amenable to thermal desorption for intermediately (and all higher) volatile compounds.	∿750-∿1,500
Porapak N (50/80 mesh)	190	175	150	N-Vinyl pyrrolidone	Vinyl pyrrolidone Pyrrolidone Pyrrilidiene	POOR (Well above system background)	1.1	Should efficiently trap intermediately (and less) volatile compounds with slightly greater affinity for polar compounds.	Very amenable to thermal desorption for intermediately (and all higher) volatile compounds.	∿750-∿1,500
Ambersorb XE-340	>400	320	300	Carbonized styrene-divinyl benzene	None observed (after conditioning at 350°C + observing on GC/MS)	GOOD (None detected above system background)	0.6	Should efficiently trap highly (and all less) volatile compounds with greater affinity for polar compounds.	Questionable amenability to thermal desorption for all but highly volatile hydrocarbons.	∿450-∿750
SKC Activated charcoal	>400	320	300	Carbonized organics	None observed	GOOD (None detected above system background)	∿0.6[c]	Should efficiently trap highly (and all less) volatile compounds with much greater affinity for polar compounds.	Questionable amenability to thermal desorption for all but highly volatile hydrocarbons.	∿350-∿600

[a] Pressure drop across tapered tubes containing 1.0 g of adsorbent at a 3-liter/min flow rate.

[b] 1 psig = 6.9 x 10^3 Pa.

[c] Estimated.

Of these five sorbents, a combination of three has been selected for use in the miniature collection system. These three sorbents are listed below along with the major reasons for their selection.

Tenax-GC - The only high temperature (400°C) adsorbent available which allows the quantitative thermal desorption of low-volatility organic compounds.

Porapak R - One of the highest capacity polymeric adsorbents with a reasonable background level (better than Porapak N) and with an overlap in range of utility (δ_m) with Tenax-GC.

Ambersorb XE-340 - Less difficulty anticipated with the desorption of compounds of intermediate volatility, fewer detrimental effects by water and reactivity with collected samples than with charcoal. Also, its range of utility (δ_m) leaves the smallest gap between polymeric and carbonaceous adsorbents in the types of compounds collected.

These sorbent materials will be packed into three separate tapered glass tubes for sampling, with flow being directed either in series or in parallel. The types of compounds that are expected to be trapped and desorbed by this sorbent package are described in Table 18 for the two modes possible. If sampling is done with the sorbent tubes in series the arrangement will be Tenax-GC at the air intake, Ambersorb XE-340 at the air exhaust to the pump, and Porapak R in the middle. In terms of total range of utility (δ_m) of the sorbent package, it should quantitatively trap and desorb compounds ranging from $\sim$450 to >2,800 (δ_m) with a possible "qualitative only" gap at $\sim$750 (δ_m).

TABLE 18. EVALUATION OF SORBENT PACKAGE FOR TWO MODES

Sorbent	Mode			
	Series		Parallel	
	Trap	Desorb	Trap	Desorb
Tenax-GC (δ_m, ∿950 to >2,800)	Quantitatively trap all low and some intermediately volatile compounds and partially (<100%) trap all other compounds.	Quantitatively desorb (almost) all compounds trapped, including those only partially trapped.	Quantitatively trap all low and some intermediately volatile compounds, and partially (<100%) trap all other compounds.	Quantitatively desorb (almost) all compounds trapped, including those only partially trapped.
Porapak R (δ_m, ∿750 to ∿1,500)	Quantitatively trap all intermediately volatile compounds passing through the Tenax, and partially (<100%) trap all other compounds passing through Tenax.	Quantitatively desorb all compounds trapped from Tenax breakthrough, including those only partially (<100%) trapped.	Quantitatively trap all low and intermediately volatile compounds, and partially (<100%) trap all other compounds.	Quantitatively desorb most of the intermediately volatile and partially trapped compounds, and partially (<100%) desorb some intermediately and low volatility compounds.
Ambersorb XE-340 (δ_m, ∿450 to ∿750)	Quantitatively trap most of the highly volatile compounds breaking through both the Tenax and the Porapak with other more volatile compounds being partially (<100%) trapped.	Quantitatively desorb most of the compounds trapped, except possibly those highly volatile compounds that border on intermediate volatility which may only partially (<100%) desorb.	Quantitatively trap all of the low and intermediately volatile compounds and most of the highly volatile compounds and partially (<100%) trap even more highly volatile compounds.	Quantitatively desorb most of the highly volatile quantitatively and partially trapped compounds, partially desorb (<100%) some intermediately (and border) volatile compounds, and not desorb (∿0%) most other compounds.

TASK 3 - DESIGN OF THE PORTABLE MINIATURE COLLECTION SYSTEM PROTOTYPE

There were a number of sampling configurations considered for use in a miniature sampling system based upon the selected sorbent materials (Tenax-GC, Porapak R, and Ambersorb XE-340). Consideration has been given to both series and parallel arrangements of the sampling tubes, and tubes of 12 mm O.D. (see Figure 20) and 17 mm O.D. were examined for this application. To determine the total pressure drop requirements for these sampling configurations, the information given in Table 19 (see also Section II.B.3) was used in the following equations.

Series

$$\text{Total } \Delta P = \text{Tenax Tube } \Delta P + \text{Por. R Tube } \Delta P + \text{Amb. 340 } \Delta P \quad (5)$$

Parallel

$$\text{Total } \Delta P = [(\text{Tenax Tube } \Delta P)^{-1} + (\text{Por. R Tube } \Delta P)^{-1} + (\text{Amb. 340 } \Delta P)^{-1}]^{-1} \quad (6)$$

The results of these calculations for different sampling configurations are given in Table 20. Note that the flow rate through each sampling tube in the parallel arrangement is only one-third of the total flow rate required through the pump. Therefore, the major pump requirement for any sampling configuration is its ability to pump at a certain flow rate over a particular pressure drop. The information given in Table 19 is plotted in Figures 21 and 22 superimposed upon the pressure drop versus flow rate (manufacturer's) specifications of a number of pumps. The pumps which are described in Figure 21 are small, light-weight models that are currently available on the market for miniature sampling applications. Data on two larger, heavier pumps are given in

TABLE 19. RESULTS OF PRESSURE DROP STUDIES ACROSS TWO DIAMETERS OF TAPERED GLASS SAMPLING TUBES

Sorbent material	Flow rate, ℓ/min	Pressure drop across 12 mm O.D. glass tube, ΔP, psig[a]	Pressure drop across 12 mm O.D. glass tube, ΔP, in. H_2O[a]	Pressure drop across 17 mm O.D. glass tube, ΔP, psig[a]	Pressure drop across 17 mm O.D. glass tube, ΔP, in. H_2O[a]
Ambersorb XE-340 (not sieved) 1.0 g	0.5	0.05	1.4	<<0.05	∿0.05
	1	0.1	2.8	<0.05	<1.4
	2	0.2[b]	5.6[b]	0.1	2.8
	3	0.6[b]	16.7[b]		
Porapak N[c] 50/80 mesh, 1.0 g	0.5	0.2	5.6	0.05	1.4
	1	0.4	11.1	0.1	2.8
	2	<0.9[b]	<25.0[b]	0.25	6.9
	3	1.1[b]	30.5[b]		
Tenax-GC 35/60 mesh, 1.0 g	0.5	<0.3	<8.3	>0.05	>1.4
	1	0.55	15.3	0.15	4.2
	2	1.1	30.5	>0.25	>6.9
	3	1.6	44.4		
Three above in series	0.5	0.5	13.9	0.1	2.8
	1	0.95	26.4	0.25	6.9
	2	2.0[b]	55.5[b]	0.5	13.9
	3	3.3[b]	91.6[b]		
Tenax-GC 35/60 mesh, ∿2 to 3 g	0.5			0.2	5.6
	1			>0.4	>11.1
	2			∿0.9	25.0

[a] 1 psig = 6.9 x 10^3 Pa; 1 in. H_2O = 2.5 x 10^2 Pa.

[b] Determined previously.

[c] Porapak R is approximately the same.

TABLE 20. TOTAL PRESSURE DROPS ACROSS DIFFERENT SAMPLING CONFIGURATIONS

Flow rate through pump, ℓ/min	Sampling arrangement: Series — ΔP total (in. H_2O[a]) = x + y + z[b]: 12 mm O.D. tubes	Series: 17 mm O.D. tubes	Series: Flow through tube, ℓ/min	Parallel — ΔP total (in. H_2O[a]) $= \left[\frac{1}{x} + \frac{1}{y} + \frac{1}{z}\right]^{-1}$[b]: 12 mm O.D. tubes	Parallel: 17 mm O.D. tubes	Parallel: Flow through tube, ℓ/min
0.5	13.9	2.8	0.5	0.99	0.35	0.17
1	26.4	6.9	1	1.95	0.76	0.33
2	55.5	13.9	2	3.98	1.55	0.67
3	91.6	-	3	8.68	-	1

[a] 1 in. H_2O = 2.5 x 10^2 Pa.

[b] Where x, y, and z represent pressure drops across the individual tubes.

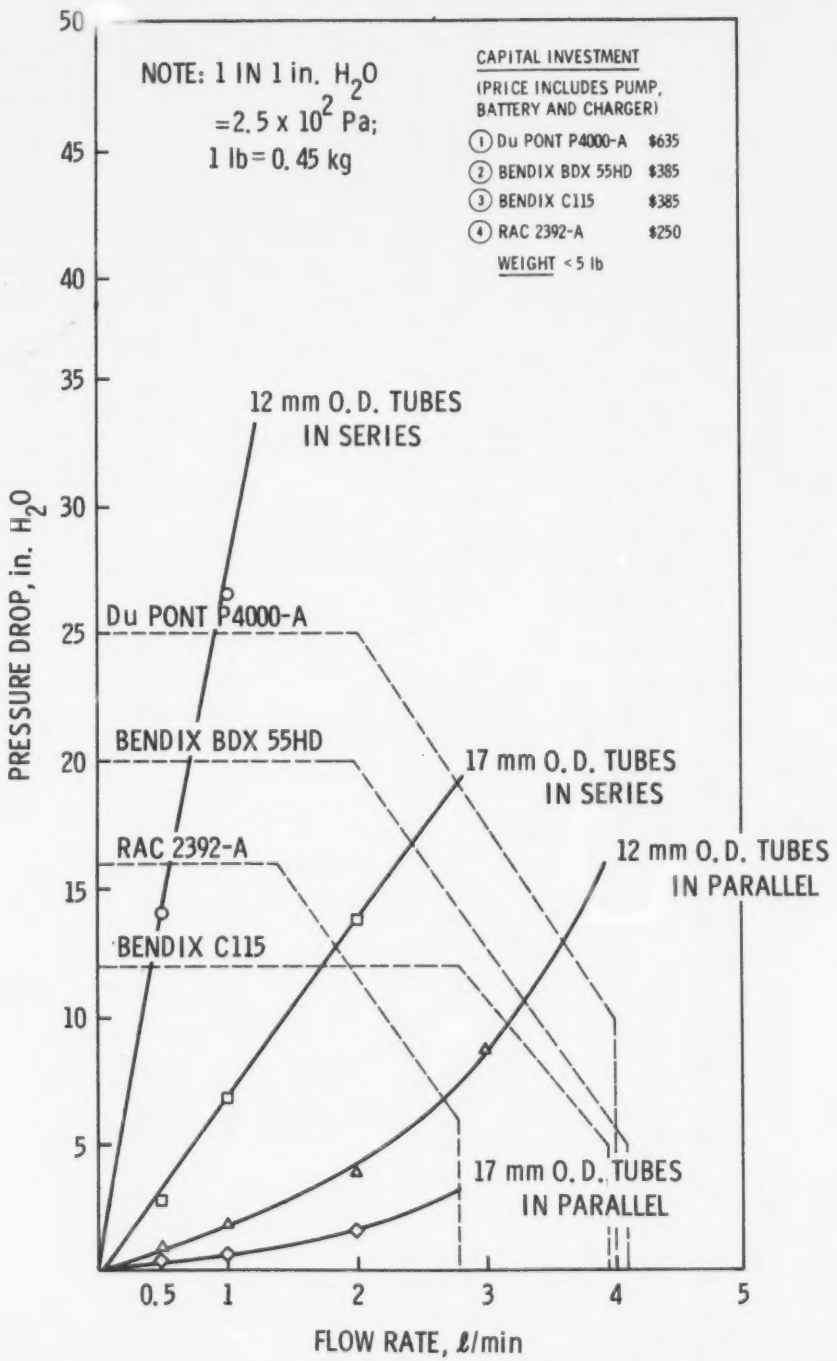


Figure 21. Plots of requirements for various sampling arrangements and the manufacturer's specifications for four miniature pumps.

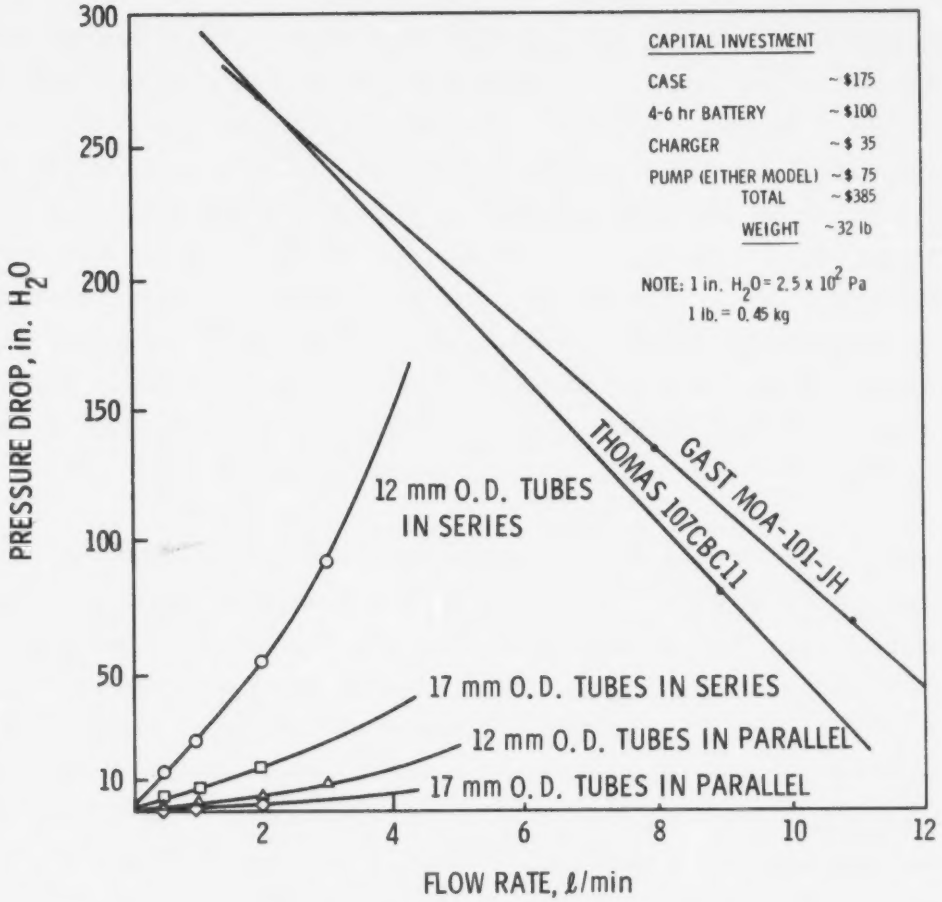
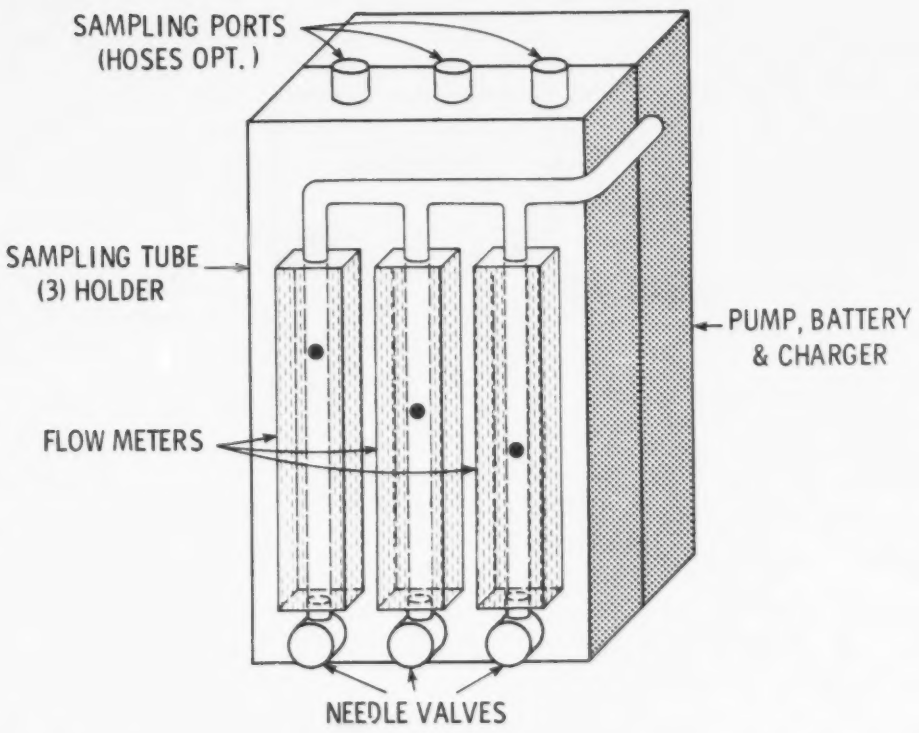


Figure 22. Plots of requirements for various sampling arrangements and the manufacturer's specifications for two large (desk-top) pumps.

Figure 22; these could be used in a "desk-top" sampling system. Some capital investment and weight information is also supplied in these figures.

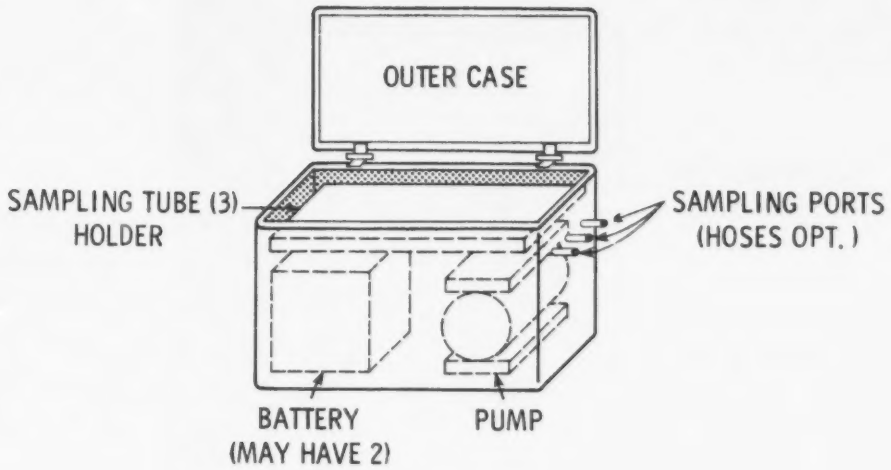
Figure 23 is a rough sketch of a possible miniature sampling system (one that would permit series or parallel sampling) and a description of its most outstanding features. This system would be small and light enough to attach to a person's belt, and would operate for 8 hours. However, it would have its flows set by delicate, easily broken needle valves and fairly inaccurate flow meters, and would be more expensive than a larger sampling system (see Figure 24). The maximum capabilities of this system are also described in Figure 23 for the four sampling configurations given in Figure 21. For example, with 12 mm O.D. sampling tubes in parallel, a maximum of about 1 ℓ/min could be passed through each tube (3 ℓ/min through the pump) across the pressure drops existing for that sampling configuration at that flow rate.

A larger, "desk-top" sampling system is similarly sketched and described in Figure 24. This model would be too bulky and cumbersome to carry for an extended period, so it would be placed on a stand, table, desk, or laboratory bench during sampling. The design of this sampler offers a number of options. For example, the power requirements may be supplied by one (lasts 4 to 6 hours) or two (lasts >8 hours) batteries enclosed in the same case as the pump and sampling tube holder or in a separate case. Power requirements may alternatively be supplied by a transformer adapted cord to a 120-V wall socket. Flow rates may be set by needle valves and flow meters (as in the smaller sampling system) or by critical orifices (which are more accurate and less easily damaged, but require more pressure drop). The maximum capabilities for the desk-top model are also described in Figure 24 for the sampling configurations in Figure 22. Higher flow rates are attainable for this model through the sorbent tubes which would permit more sample to be collected. Whether or not this increase



Weight	- 2.3 kg (<5 lb)
Cost	- $635 for DuPont P4000-A (pump, battery and charger only)
Size	- 2 or 3 times the size of most pocket calculators
Operational time	- ≥8 hours
Method of setting flow	- Needle valves and small flow meters
Durability problems	- Needle valves fragile and pump near max for long periods
Capabilities (max)	- Series, 12 mm O.D. tubes - 0.5 ℓ/min
(*preferred)	- Series, 17 mm O.D. tubes - 2 to 2.5 ℓ/min
	*Parallel, 12 mm O.D. tubes - 1 ℓ/min
	Parallel, 17 mm O.D. tubes - 1 ℓ/min

Figure 23. Sketch and description of small personnel sampler.



Weight	- ∿14.5 kg [∿32 lb; ∿27 kg (∿60 lb) if 2 batteries]
Cost	- ∿$385 (for case, 1 battery, charger and pump only)
Size	- 33 cm (13 in.) long, 20 cm (8 in.) wide, ∿13 cm (5 in.) deep
Operational time	- 4-6 hr (>8 hr with 2 batteries or wall adapter)[a]
Method of setting flow	- Needle valves and flow meters or critical orifices[b]
Durability problems	- Needle valves (if used) fragile
Capabilities (max) (*preferred)	- Series, 12 mm O.D. tubes - 4 to 5 ℓ/min Series, 17 mm O.D. tubes - 7 to 8 ℓ/min *Parallel, 12 mm O.D. tubes - 2.5 to 3 ℓ/min Parallel, 17 mm O.D. tubes - 3.5 to 4 ℓ/min

[a]Battery may be put into a separate pack and/or a 120-V line with transformer may be used to adapt this sampler to a wall socket.

[b]Due to pressure drop required at orifices the capabilities would be reduced.

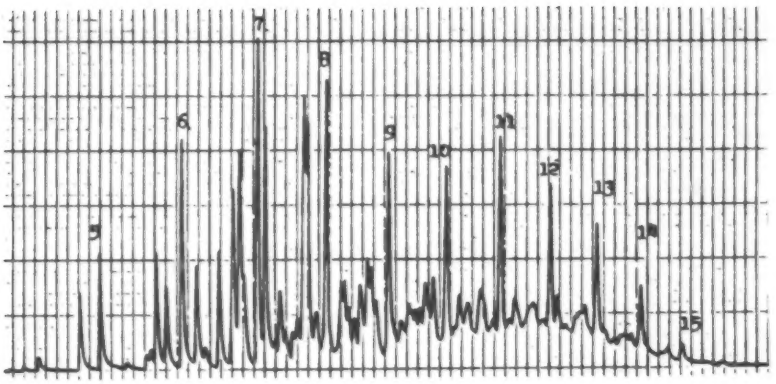
Figure 24. Sketch and description of large desk-top sampler.

in sample will significantly improve analytical sensitivity will be investigated to determine if the desk-top model, with its disadvantages of cumbersome size and weight, should be used in this project. The final design of the portable miniature collection system will be completed during the second year of this contract as part of Phase II, in order to permit discussion of design options with the EPA.

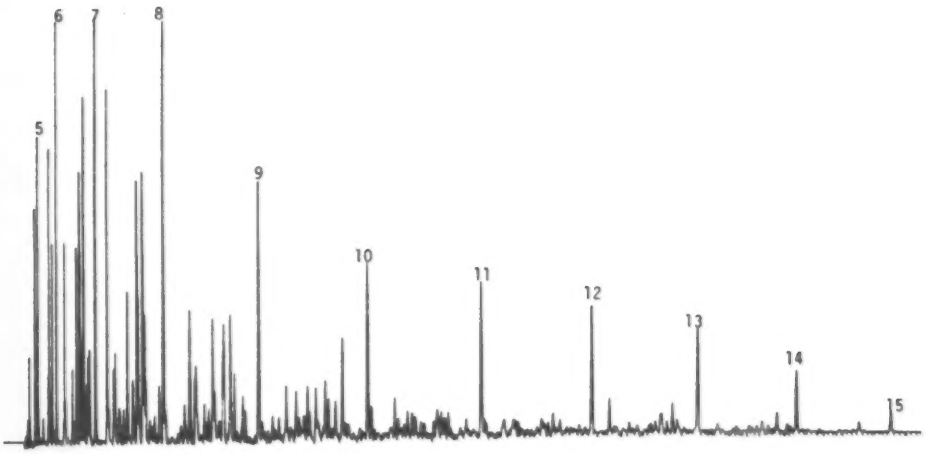
ADDITIONAL WORK - ANALYTICAL DEVELOPMENT

During this contract year a Hewlett-Packard Model 5840A GC with glass capillary option was purchased for use in the development of analytical techniques during Phase II of this research program. After the initial setup of this instrument, a Perkin-Elmer, 100-meter SF96 WCOT column was installed. To demonstrate the analytical capabilities of this system, samples of a highly complex organic mixture (JP-4 jet fuel) were analyzed. Figure 25 contains two chromatograms. Chromatogram A is from an analysis of JP-4 done previously with a packed column. Chromatogram B is an analysis of JP-4 done on the capillary GC system at a flow rate of 1.2 mℓ/min of nitrogen and a sample split of about 200 to 1. The increased resolution of the capillary column is readily apparent.

Work was continued in the area of analytical development with the design, construction, and installation of a special capillary inlet system. This system was made to permit the thermal desorption of sampling tubes, reconcentration of the desorbed sample in a trap, and introduction of the sample into the capillary GC for analysis. In order to install this special capillary inlet system (desorption chamber, valve, and trap) it was first necessary to make two modifications to the HP 5840 GC. The first modification involved the installation of an auxiliary "desorption" carrier for use during the thermal desorption of sorbent tubes. This auxiliary desorption carrier was directed through an



A. JP-4 separated by a packed column.



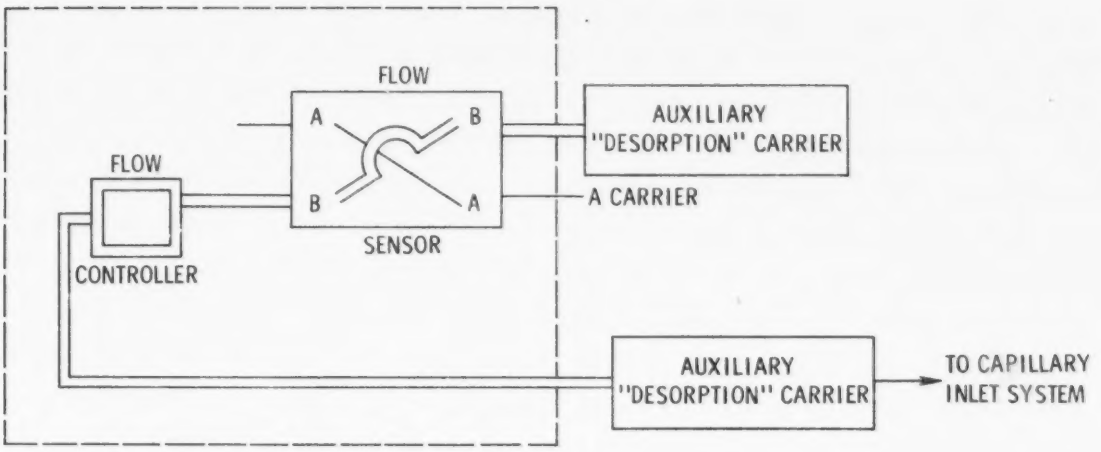
B. JP-4 separated by a SF96 WCOT column.

Figure 25. Two chromatograms of JP-4 jet fuel. Numbered peaks are the n-alkanes of corresponding carbon number.

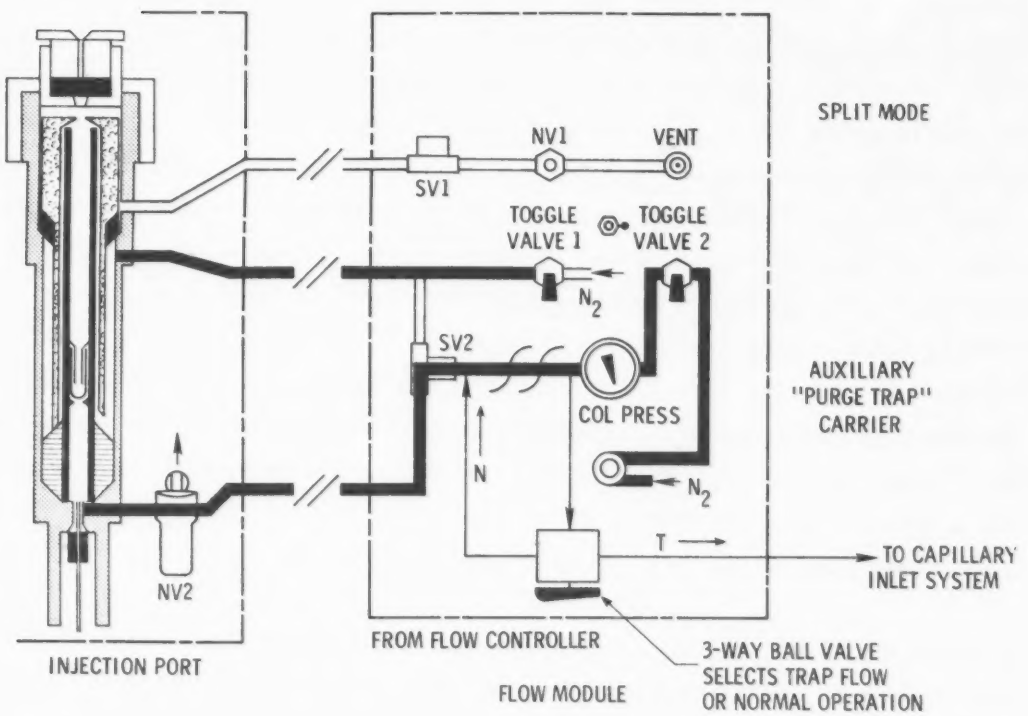
available flow sensor on the 5840 so that the flow could be monitored directly. This modification is shown in Figure 26, A. The second modification (Figure 26, B) involved the installation of a three-way [3.2 mm (1/8 in.) swage] ball valve within the capillary flow system to allow for the selection of either a "normal injection" flow pattern or a "purge trap" flow pattern. In the "purge trap" flow pattern a source of carrier is diverted from the normal flow pattern and directed into the capillary inlet system. This provides a source of carrier for sweeping the capillary trap when it is switched into the analyze position (i.e., into the flow system with the capillary column).

The current configuration of the capillary inlet system is sketched in Figure 27. This inlet system performs three major functions. The first function is the thermal desorption of sorbent tubes and is accomplished by a copper tube furnace wrapped with Nichrome heating wire. The temperature of this tube furnace is controlled by a Variac and read with a digital voltmeter. Flow selection and direction is the second major function of the inlet system. This is accomplished with a six-port, two-position valve within a heated oven compartment. The other function of cryogenic trapping and focusing of the desorbed sample is accomplished in a 1-m, 0.8 mm (0.03-in.) I.D. transaxially coiled nickel trap that is cooled by liquid nitrogen during sample collection and heated by electrical resistance during sample introduction to the capillary column. Thermocouples are attached to a pyrometer to permit monitoring the temperatures of the valve, valve oven, and trap.

A flow diagram of the capillary inlet system is shown in Figure 28 for the two valve positions. In the "trap" position a sorbent tube is desorbed by the tube furnace and its sample is swept by the auxiliary "desorption" carrier through the valve into the nickel capillary trap, which is 50% submerged in liquid nitrogen. The flow out of the trap is passed through the "A" injection port

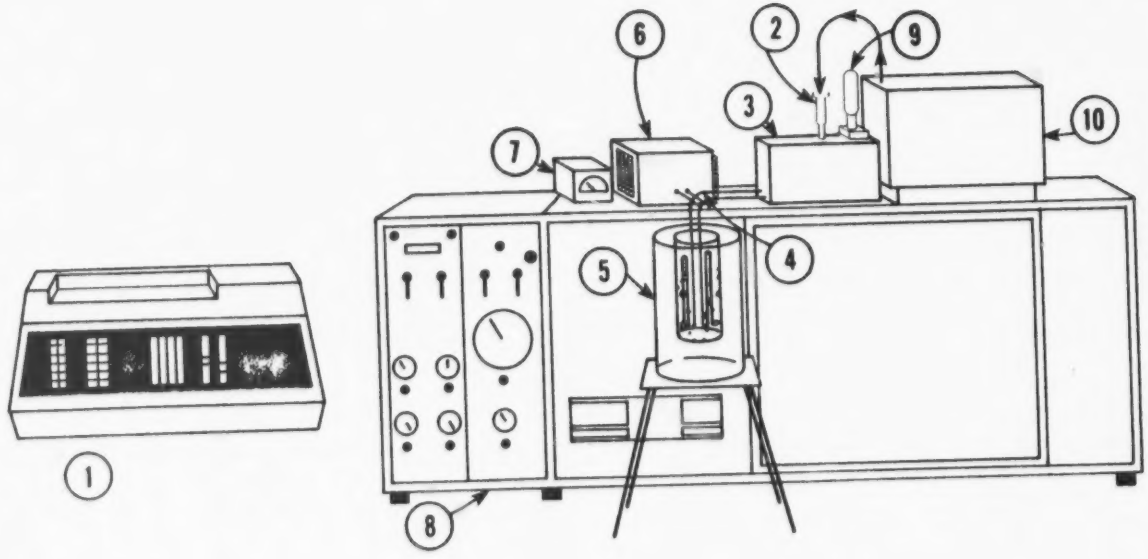


A. Auxiliary "desorption" carrier modification.



B. Auxiliary "purge trap" modification.

Figure 26. Flow schematics of two GC modifications



1. HEWLETT-PACKARD MODEL 5840A GC WITH GLASS CAPILLARY OPTION
2. TUBE DESORPTION CHAMBER
3. HEATED VALVE OVEN-CONTAINING 6-PORT, 2-POSITION, LOW DEAD VOLUME VALVE
4. 1-METER, Ni CAPILLARY TRANSAXIAL TRAP
5. DEWAR CONTAINING LIQUID N_2 FOR COOLING CAPILLARY TRAP
6. TRANSFORMER FOR INSTANT HEATING OF CAPILLARY TRAP
7. PYROMETER FOR TEMPERATURE READINGS
8. FLOW CONTROLLERS AND SPLIT CONTROLLER
9. RECOLLECTION VENT WITH TUBE
10. DETECTOR ADAPTABLE TO FID, N-P FID, GLASS JET FID

Figure 27. Capillary GC with capillary inlet system.

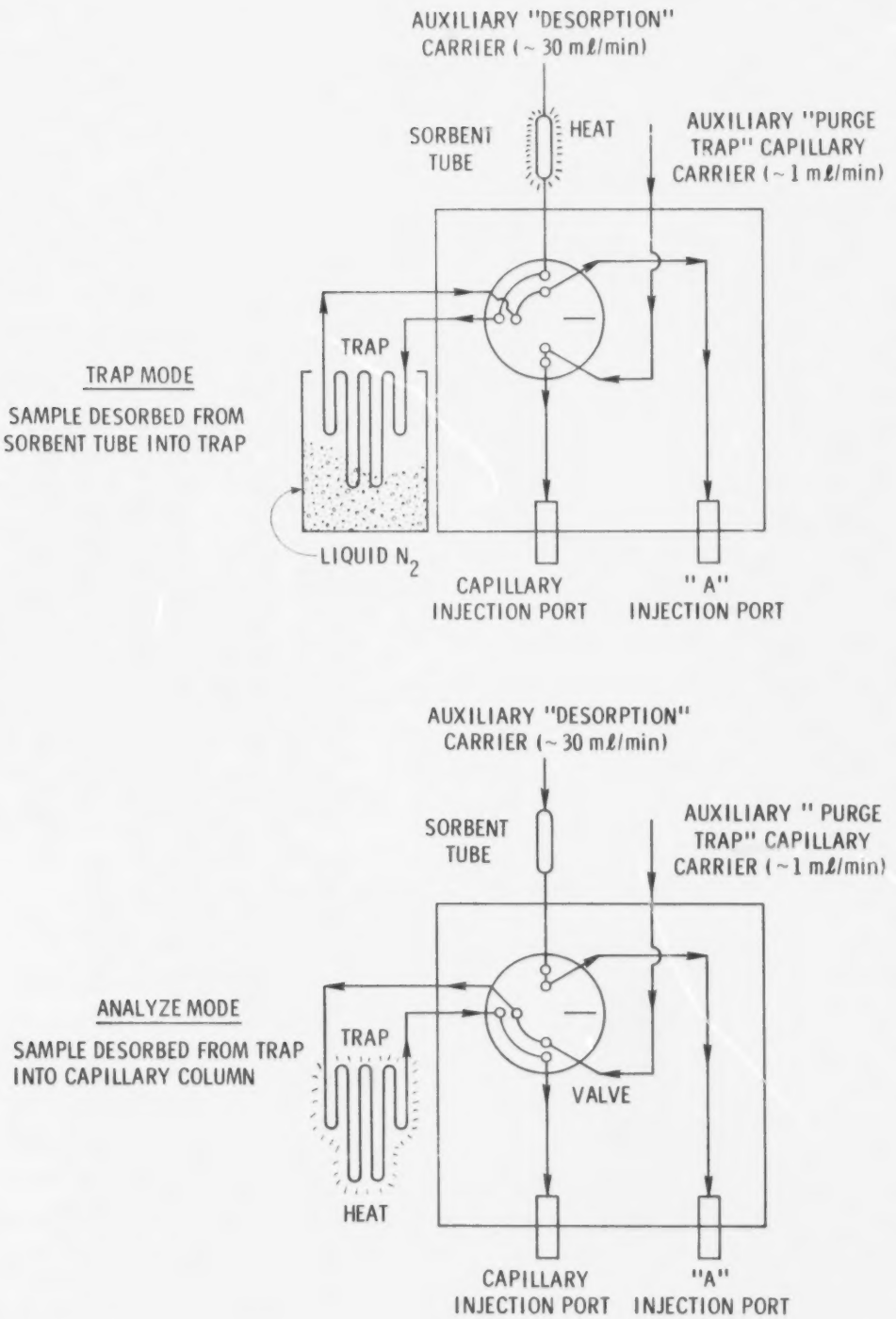


Figure 28. Flow schematic of capillary inlet system.

to the "A" FID for monitoring trap breakthrough. When the valve is switched to the "analyze" position, simultaneously the tube furnace is cooled, the liquid nitrogen is removed from the trap, and the trap is heated. The auxiliary "purge trap" flow then sweeps the collected sample out of the trap and into the capillary injection port. When the capillary GC is operated in the "split" mode, most of the sample entering the injection port is vented, and only a small portion enters the capillary column for chromatographic separation and analysis. A modification has been made to re-collect the vented portion of a sample onto another sorbent tube for additional, subsequent analyses. A more refined, neatly packaged, and conveniently operated version of the capillary inlet system is anticipated after evaluations and modifications are completed.

Some preliminary evaluations of the capillary inlet system on the capillary GC were conducted to determine the utility of this system. To permit initial evaluations of this system by sample injection, a 0.6 cm (1/4 in.) swage tee was installed at the base of the tube furnace, capped with a septum nut, and wrapped with heating tape. For all capillary inlet system evaluations, the flow out of the trap was monitored by the "A" FID during sample trapping to assure that no breakthrough occurred. The "B" FID (glass capillary) was monitored during sample analysis. For injected samples of ether, no breakthrough was noted on the "A" FID when the nickel capillary trap was cooled, but immediate breakthrough occured when it was not cooled. Similar samples of pentane and hexane were also analyzed with optimistic results. Injected samples of JP-4 were then analyzed for comparison with earlier, regularly injected samples (see Figure 25). Two nickel traps were compared in these analyses which were of different, [0.8 and 1.6 mm (0.03 and 0.04 in.)] internal diameter but otherwise identical. Both analyses indicated slight peak broadening and poorer resolution compared to previous samples, but of the two traps, the 0.8 mm (0.03 in.) I.D. trap was judged to yield

slightly better results. A chromatogram of a JP-4 analysis with the smaller diameter trap is shown in Figure 29.

Next, a six-component mixture containing pentane, hexane, heptane, octane, benzene, and toluene was obtained and evaluations conducted with this mixture. The analysis of an injected sample of this mixture is depicted in chromatogram A of Figure 30. Additionally, samples of this six-component mixture were generated using Monsanto Research Corporation's sample generation system (see Appendix A) and collected on Ambersorb XE-340 sorbent sampling tubes (1 g of sorbent). An analysis of a 1-ℓ/min, 16-hr sample is shown in Figure 30, B, and was accomplished using a 30-min sorbent tube desorption with nickel capillary trap collection and a 5-min nickel capillary trap desorption. For some sorbent tube samples, the vented (500:1 split) portions were re-collected on other sorbent tubes at the capillary GC splitter. The analysis of one of these re-collected samples is shown in Figure 30, C. (The additional peaks in Figure 30, C, are from residual contamination at the splitter vent outlet.) Re-collected samples showed an average of 93% of the original sample amount if analyzed the same day as collection. Re-collected samples stored for a day or two showed between 40% and 67% of the original sample, with refrigeration showing no effect.

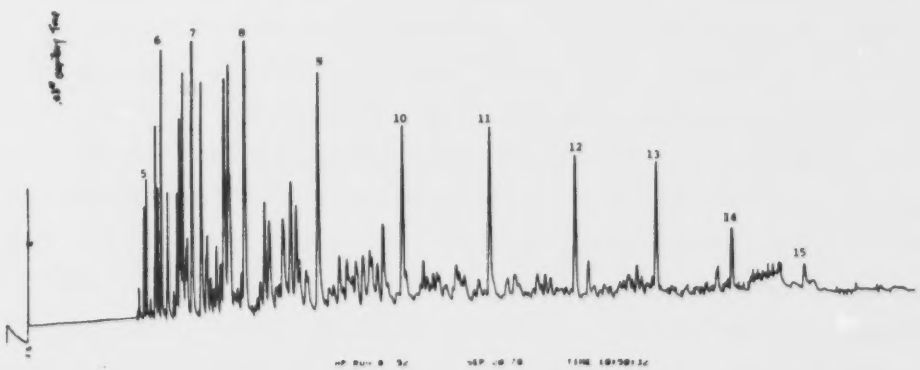
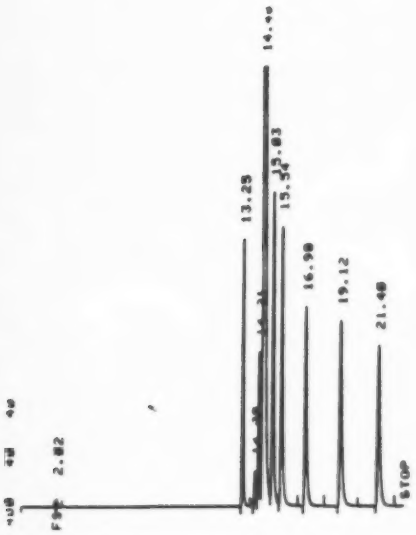
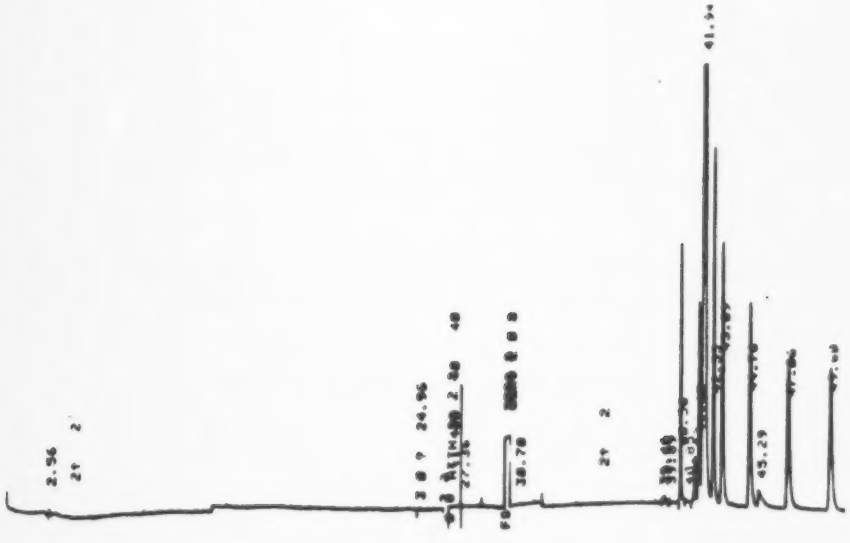


Figure 29. Injections of JP-4 into a 0.8 mm (0.03 in.) diameter, liquid N_2 cooled capillary trap, and desorption of trapped sample into a SF96 WCOT column for analysis.

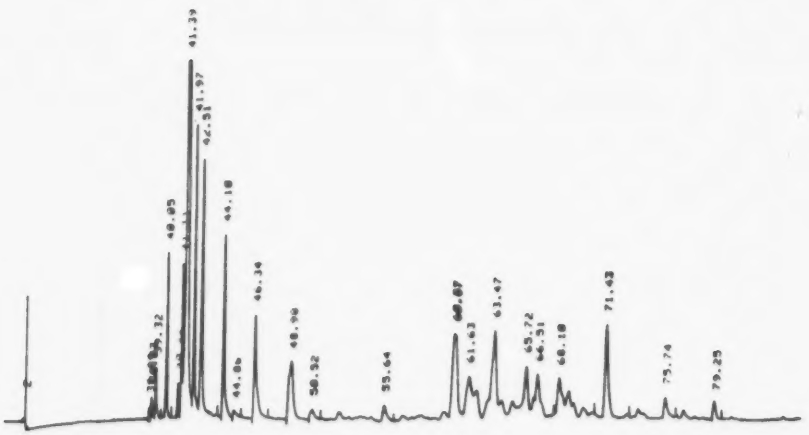


A. Injected sample of six-component mixture.



B. Sample of six-component mixture from an Ambersorb XE-340 sorbent tube generated by the sample generation system.

Figure 30. Evaluation of capillary inlet system with samples of a six-component mixture (pentane, hexane, benzene, heptane, toluene, and octane), collection in liquid N_2 cooled trap, and desorption into a SF96 WCOT column for analysis.



C. Sample of six-component mixture from an Ambersorb XE-340 sorbent tube collected from the capillary GC splitter.

Figure 30 (continued)

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APPENDIX A

STANDARD SAMPLE GENERATION SYSTEM

In order to evaluate the sorbent sampling systems used in this project it is necessary to have a method for generating known concentrations of organic compounds in dynamic gas streams. MRC has developed a dynamic standard sample generation system based on the controlled syringe injection of organic liquids into a flowing stream of gas (N_2), followed by vaporization and subsequent dilution.

Figure A-1 is a schematic diagram of the sample generation system. The main frame of the system is a modified F&M Model 700 gas chromatograph. The chromatograph has been stripped of the protective metal covering and the detector has been removed. The oven [30.5 cm x 30.5 cm (12 in. x 12 in.)] was relocated from the right to the left side of the main frame. Four heated zones were available on the original GC. One of these zones controls the oven temperature while the other three are available for heating various components of the sample generation system. Two of these are used to separately control the temperature of the two three-port injection blocks (see Figure A-1). The final zone is available for heating transfer lines for direct interfacing with a detector for frontal analysis capacity studies. A Simpson pyrometer (0°C to 500°C) has been added along with a selection switch and necessary circuit modifications to allow the monitoring of temperatures in the four zones.

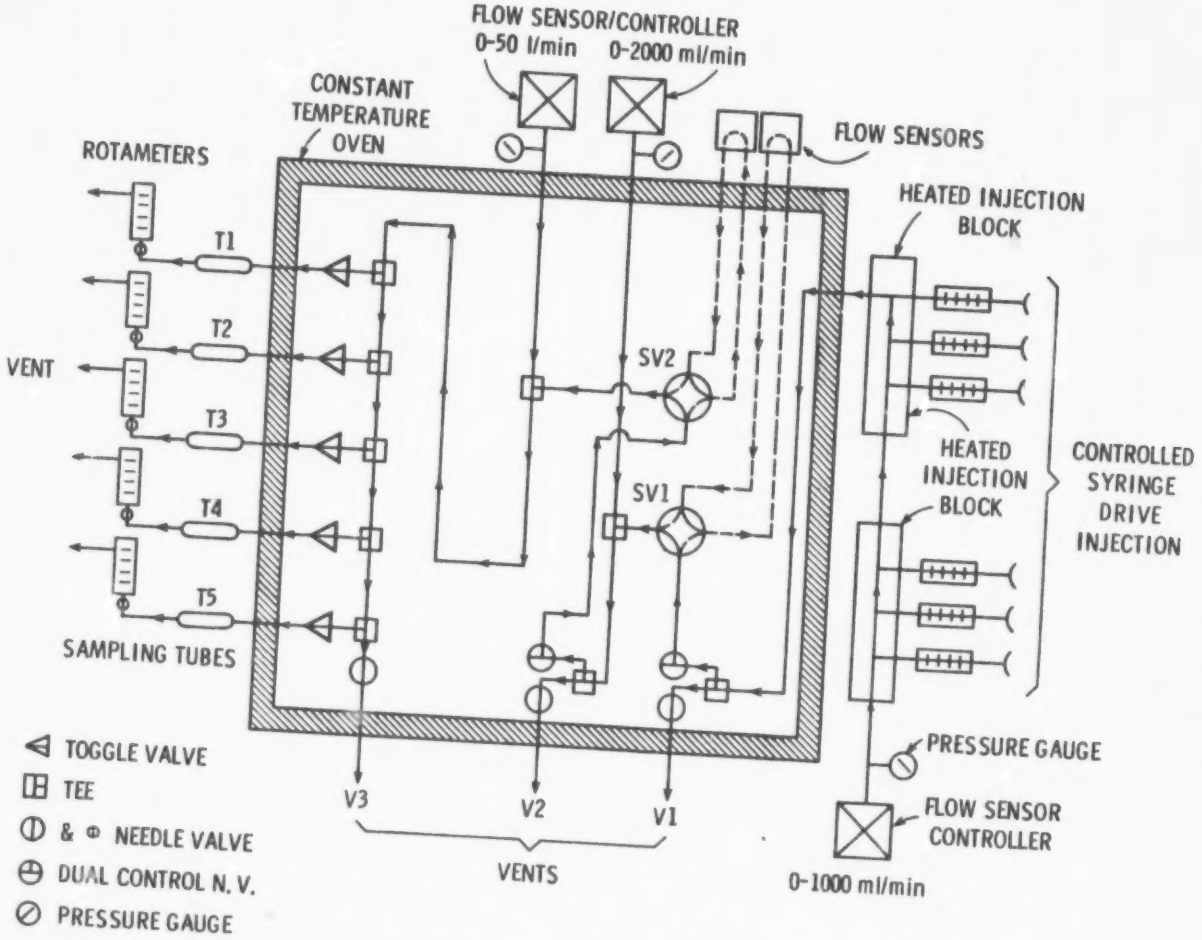

Figure A-1. Standard sample generation system.

A 45.7 cm x 45.7 cm x 0.6 cm (18 in. x 18 in. x 1/4 in.) aluminum plate has been attached to the mainframe to the right of the oven to accommodate the syringe drives. The necessary bulkhead fittings, tees, toggle valves, needle valves, tubing, pressure gauges, and rotameters were also added to accomplish the configuration indicated in Figure A-1. Materials of construction for the flow system are either stainless steel or nickel. The entire system is contained in a 2.4 m x 1.2 m x 1.5 m (8 ft x 4 ft x 5 ft) exhaust hood with access at both front and back through double sliding doors. The flow control/sensing instrumentation, pressure gauges, and rotameters are mounted on a panel and rack assembly in the hood above the generation system.

The generation system functions in the following manner. A source of carrier gas (N_2) is introduced and split into primary, secondary, and tertiary flows. The primary flow passes through a Brooks Model 5841 mass flow sensor/controller which maintains the flow at a preset value (0 to 1,000 mℓ/min). This flow passes through individually heated and controlled injection blocks which are designed to each accept three syringes mounted on Sage Model 355 variable control syringe drives. This allows for simultaneous introduction of six pure liquid components or potentially many more if mixtures of compounds are used in the syringes. The rate of injection can be varied from submicroliter-per-hour to milliliter-per-minute rates by choice of syringe size and drive rate. The liquid samples are vaporized in the injection blocks and swept with the carrier gas into a constant temperature oven.

The major portion of the primary flow passes through the oven, through a needle valve used to regulate the pressure in the primary flow path, and is expelled to a vent (V1). A small portion (usually ∿10 mℓ/min) of the primary flow is split off through a dual control needle valve and passes into a switching valve (SV1). This valve is actually one-half of an eight-port switching valve. The second half is used for an identical function in

the second dilution stage. The switching valve makes it possible to switch a Brooks Model 5810 (0 to 100 mℓ/min) mass flow sensor into the flow path (dashed line in Figure A-1) to measure the exact split on the primary flow. Once the split has been established, the flow sensor is switched out of the system so that the sensing elements are not subjected to sample containing organic vapors. The split is maintained by carefully controlling the pressures in each of the dilution stages.

The pressures are monitored with Heise Model CM precision pressure gauges [0 to 6.9 x 10^5 Pa (0 psi to 100 psi)]. By maintaining a constant pressure in each of the dilution stages a constant pressure differential is established between the stages assuring a consistent split ratio across the needle valves.

The portion of the primary flow that is split out passes from the switching valve and is combined with the secondary carrier flow which enters the constant temperature oven through a Brooks Model 5841 mass flow sensor/controller (0 to 2,000 mℓ/min). As in the case of the primary flow, the major portion of the secondary flow passes through the oven and is expelled to vent V2 through a needle valve. A small portion (usually 10 mℓ/min) of the secondary flow is split off through a dual control needle and passes into a switching valve (SV2). This valve functions in an identical manner to valve SV1 to place a second Brooks Model 5810 (0 to 100 mℓ/min) mass flow sensor into the flow path for measuring the second split.

The portion of the secondary flow that is split out passes from the switching valve and is combined with the final dilution stream which enters the constant temperature oven through a Brooks Model 5841 mass flow sensor/controller (0 to 50ℓ/min). This final concentration is available for sampling through a five-port manifold system that will accommodate sorbent sampling tubes. The sampling rates through the sorbent tubes are maintained

by Brooks Model 1110 rotameters at the exit of the tubes. The unused portion of the final dilution stage is expelled to vent V3.

With the sample generation system in this configuration it is theoretically possible to achieve dynamic sample generation of pure compounds down to low ppt concentrations. For example, a concentration of ∿4 ppt should be achievable using pure benzene in a 25-µℓ syringe at a syringe drive rate of 25% of the 1/1,000 of full range setting and dilution stage flows of 1,000 mℓ/min, 2,000 mℓ/min, and 50 ℓ/min, respectively, using 10 mℓ/min splits from both the first and second dilution stages. Under these conditions, the syringe drive mechanism delivers 0.0143 µℓ/min.